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- This report provides general guidance to Corps of Engineer Division and District personnel on the design and conduct of programs for monitoring chemical contaminants in reservoir waters, sediments, and biota. The report is organized based on eight areas of consideration in conducting a reservoir contaminant monitoring program: (a) historical water quality concerns in Corps reservoirs, statutes relevant to reservoir management, and existing contaminant problems in

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20. ABSTRACT (Continued).

Corps reservoirs; (b) selection of variables to be monitored; (c) design of the sampling program, including location and frequency of sampling and statistical considerations; (d) sampling methods and quality assurance procedures; (e) analytical methods; (f) procedures for management of monitoring programs conducted under contract; (g) management and processing of data; and (h) data interpretation, including statistical considerations and compliance with regulatory criteria and standards.

It is emphasized that the general recommendations provided in the report must be tailored to the design, morphometry, and operation of a specific reservoir and the specific contaminant problems that are known or suspected to occur there.

PREFACE

This report was sponsored by the Office, Chief of Engineers (OCE), US Army, as part of the Environmental and Water Quality Operational Studies (EWQOS) Work Unit IIC.1, entitled Operational and Management Strategies for Reservoir Contaminants. OCE Technical Monitors for EWQOS were Dr. John Bushman, Mr. Earl Eiker, and Mr. James L. Gottesman.

Work for this report was conducted during the period August 1983 through July 1984 by Mr. Jack B. Waide, Water Quality Modeling Group (WQMG) of the Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES). The draft report was reviewed by Drs. James M. Brannon, Robert M. Engler, Douglas Gunnison, and Robert H. Kennedy, all of EL.

The study was conducted under the direct supervision of Dr. Thomas L. Hart, Chief, Aquatic Processes and Effects Group, and Mr. Mark S. Dortch, Chief, WQMG, and under the general supervision of Mr. Donald L. Robey, Chief, Ecosystem Research and Simulation Division, and Dr. John Harrison, Chief, EL, WES. Program Manager of EWQOS was Dr. Jerome L. Mahloch, EL. The report was edited by Ms. Jessica S. Ruff of the WES Publications and Graphic Arts Division.

Director of WES was COL Allen F. Grum, USA. Technical Director was Dr. Robert W. Whalin.

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CONTENTS

GENERAL GUIDELINES FOR MONITORING
CONTAMINANTS IN RESERVOIRS

PART I: INTRODUCTION

Background

Water quality concerns in reservoirs

1. The US Army Corps of Engineers (CE), through its Civil Works Program, is charged with the planning, design, construction, and operation of a wide variety of water resources projects. Among these projects are over 500 reservoirs that are either in operation or under planning or construction. These projects are operated for many purposes, including flood control, water supply, hydroelectric power generation, navigation, recreation, fish and wildlife conservation, and low-flow augmentation. Some reservoirs are operated for only a single purpose; others, however, are authorized as multiple-purpose reservoirs. This may result in conflicting uses for reservoir storage, requiring operators to be concerned with compatibility among project purposes.

2. The operation of a reservoir project must be consistent with its authorized purpose(s). Historically, project operation has been concerned primarily with issues relating to water quantity management. Recently, however, reservoir management and operation have involved issues related to water quality in addition to water quantity. This concern is the result of changes over the past 15-20 years in the public's perception of the importance of environmental quality as a general societal goal, as well as specific legislation at State and National levels which specifies water quality goals to be met by water resource managers, Executive Orders that have reinforced specific statutes, and litigation against the CE and other Federal agencies charging noncompliance with specific sections of Federal statutes.

3. The most important legislation passed during this period relating to water quality management includes the Federal Water

Pollution Control Act Amendments of 1972 (Public Law (PL) 92-500), which required Federal agencies having jurisdiction over any activity resulting in the discharge or runoff of pollutants to comply with the substantive requirements of Federal, State, interstate, and local laws for pollution abatement, and the Clean Water Act of 1977 (PL 95-217), which further required Federal agencies to meet both substantive and procedural requirements of pollution abatement laws and allowed citizens to sue for noncompliance. Executive Order 11752 (1973) reinforced PL 92-500 by directing Federal agencies to provide leadership in meeting the goal of protecting and enhancing the quality of the Nation's water resources. Similarly, Executive Order 12088 (1978), which revoked Executive Order 11752, reinforced PL 95-217 by mandating compliance with Pollution Control Standards. As a consequence of these trends, the importance of environmental and water quality considerations to the design, operation, and management of reservoirs has become well established.

4. During the same period the above changes were taking place, identification of the water quality constituents or variables of primary management interest has undergone similar change and redefinition. Initially, water temperature, especially of project releases, was the variable of prime management concern. Considerable effort has been expended, for example, to design multilevel outlet structures in order to meet release temperature objectives. Subsequently, environmental concern broadened to include consideration of dissolved oxygen and other water quality issues related to oxygen depletion in reservoir hypolimnia (e.g., anaerobic conditions and sediment releases of plant nutrients and reduced chemical species). Management options have included such mitigation measures as reaeration of project releases, artificial destratification, localized mixing, and hypolimnetic aeration.

5. Increased public awareness of environmental quality issues has resulted in a further broadening of the reservoir management issues to include eutrophication, e.g., increased nitrogen and phosphorus loadings to reservoirs, algal blooms, and taste and odor problems. Although the range of environmental and water quality issues associated with reservoirs has expanded due to environmental legislation, management

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techniques for dealing with these issues are constrained due to operational requirements of the authorized project. Moreover, meeting water quality objectives related to one project purpose may compromise objectives associated with other authorized purposes, further complicating the management process.

6. Recently, a further expansion of water quality concerns in CE reservoirs has begun to develop, related to the possible occurrence of toxic chemical contaminants, both metals and organic compounds, in reservoir waters, sediments, and biota. This expansion coincides with a general scientific and public concern regarding the presence and impacts of toxic contaminants dispersed throughout the environment. The extent and magnitude of possible contaminant problems in CE reservoirs are unknown. Moreover, basic processes regulating the transport, fate, and effects of toxic contaminants in reservoirs remain poorly understood. Nonetheless, this represents another important expansion of reservoir water quality concerns, and means that new types of operational restrictions on reservoir management may need to be considered in the future. If contaminant issues become more important to reservoir management, then meeting water quality criteria may become more difficult. Also, because of the risks to human and aquatic populations posed by contaminants, the criteria themselves may become more stringent in the future.

Water quality criteria and standards

7. Although the importance and environmental impacts of potential contaminant problems in CE reservoirs are just beginning to be understood, the general concern with contaminants in the Nation's water resources has led to the establishment of a number of water quality criteria and standards relevant to the regulation of reservoir contaminants. Together with field sampling data on contaminant levels in reservoir waters, sediment, and biota, these criteria and standards form the basis for deciding whether contaminant problems exist in CE reservoirs and how extensive such problems might be. For the purposes of this report, the criteria and standards discussed in the following paragraphs are the most important. The specific chemical contaminants

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covered by these criteria and standards will be discussed further in Parts II and VIII of this report.

8. In response to the Clean Water Act of 1977 and a related court order, the US Environmental Protection Agency (EPA) published water quality criteria for 65 toxic pollutants affecting human health and aquatic life (US EPA 1979a; Federal Register, 1980, Vol 45, pp 79318-79379). These criteria are based on the best scientific knowledge currently available; however, they have no regulatory impact by themselves. They are, however, the basis for many State water quality standards that are enforced by State pollution control agencies. Criteria proposed for the regulation of human health are estimates of ambient water concentrations which represent either safe levels for humans (noncarcinogens) or various levels of incremental risk (carcinogens). Criteria for the protection of aquatic life were proposed in the form of both a 24-hr average and a maximum water concentration. The 24-hr average value corresponds to an estimate of the maximum chronic exposure that can be tolerated by an aquatic organism, while the maximum value estimates the maximum tolerable acute exposure.

9. In response to the Federal Water Pollution Control Act Amendments of 1972, the EPA published water quality criteria, again based on the best scientific evidence available at that time, which were designed to protect the health and welfare of humans, plankton, fish, shellfish, wildlife, plant life, shorelines, beaches, and aesthetic and recreation resources (US EPA 1976). Referred to as the EPA 1976 Red Book criteria, these water quality criteria formed the basis for water quality standards that are still in effect in many States. However, the States are gradually changing their standards to conform to the 1980 criteria. State standards may also reflect local conditions, such as projected water uses, background levels of specific contaminants, presence of sensitive biota, and local hydrometeorological conditions. Some States have nonspecific standards for contaminants, while others follow the 1976 or 1980 EPA criteria exactly (Khalid et al. 1983).

10. The US Public Health Service (PHS), under authority of the PHS Act as amended by the Safe Drinking Water Act (PL 93-523), published

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the National Drinking Water Standards, comprised of primary and secondary standards (Code of Federal Regulations (CFR) 1980, Vol 40, Parts 141 and 143). Primary standards for both inorganic and organic chemicals in drinking water at the tap went into effect in 1977, while secondary standards for other variables went into effect in 1981. The limits proposed in the Drinking Water Standards differ in many cases from the EPA criteria, for two reasons (Khalid et al. 1983). First, as required by PL 93-523, these standards take into consideration issues related to technical and economic feasibility of compliance, whereas the EPA criteria do not consider such issues. Second, the basic risk model underlying the Drinking Water Standards differs from that which forms the basis for the EPA criteria. EPA's water quality criteria were not intended as drinking water standards.

11. Finally, the US Food and Drug Administration (FDA) has established maximum concentrations of contaminants in the tissues of select aquatic species likely to be ingested by human populations (US FDA 1979). Fewer contaminants are covered by the FDA regulations than by the criteria and standards summarized here.

CE response to
water quality concerns

12. In response to the environmental and water quality concerns enumerated above, the CE has issued a number of specific Engineer Regulations (ER), including the following:

a. ER 1110-2-240, "Water Control Management," which delineates overall policy and procedures required for implementing CE responsibilities for water control management.

b. ER 1130-2-334, "Reporting Water Quality Management Activities at Corps Civil Works Projects," which establishes water quality considerations as an integral part of CE responsibilities for water control management and delineates requirements for the monitoring and reporting of water quality activities at CE projects.

c. ER 1130-2-415, "Water Quality Data Collection, Interpretation, and Application Activities," which establishes guidelines for activities involving the collection, interpretation, and application of water quality data associated with water control management of CE projects.

13. Another CE response to the water quality concerns discussed previously involved sponsoring several water quality sympos. ... which collection, interpretation, and evaluation of water quality data at CE reservoirs were discussed (Committee on Water Quality 1977, 1978, 1980, 1982, 1984). Also, in 1978, the Office, Chief of Engineers (OCE), initiated a major research program, Environmental and Water Quality Operational Studies (EWQOS) (Keeley et al. 1978). Research conducted under the EWQOS Program has addressed a variety of reservoir water quality issues with the purpose of developing design and operational guidance for achieving water quality objectives in a manner that is compatible wit. project purposes. Many of the results related to reservoirs are summarized in EM 1110-2-1201, "Reservoir Water Quality."

Survey of reservoir
contaminant problems

14. One component of the EWQOS Program, Work Unit IIC: Operational and Management Strategies for Reservoir Contaminants, involved conducting an initial survey of contaminants in CE reservoirs. The purpose of this survey was to review, analyze, and interpret existing data on the nature and magnitude of chemical contaminants in CE reservoirs, and to suggest interim guidelines for operational and management techniques useful for minimizing existing contaminant problems. These guidelines were to be based on current knowledge of contaminant behavior in aquatic environments. Thus, an ancillary purpose of this study was to survey information on major processes affecting the transport, persistence, and bioavailability of contaminants in reservoirs and their tributaries (Khalid et al. 1983).

15. Information for this survey was compiled from a variety of sources, including the EPA STORET data base system, published and unpublished literature, and direct contacts with CE Division and District personnel. Once available data were assembled, they were analyzed statistically and compared to water quality criteria and standards summarized previously. Because the data were assembled prior to publication of the 1980 EPA criteria, the water quality criteria proposed by the EPA in 1979 and the 1976 Red Book criteria for water concentrations

along with the FDA limits on tissue concentrations for edible freshwater species were taken as the relevant standards for identifying CE reservoirs with potential contaminant problems. Khalid et al. (1983) defined a problem reservoir as one for which the reported concentrations of one or more contaminants exceeded either or both the 1979 EPA proposed criteria and the FDA guidelines. Results of this survey would not have changed substantially had the 1980 EPA water quality criteria been available for identifying potential reservoir problems.

16. Data on contaminant levels were assembled for 109 reservoirs located in nine of the ten CE Divisions (Khalid et al. 1983). Of these reservoirs, 71 (65 percent) were identified as having potential contaminant problems. That is, the reported concentration of one or more contaminants exceeded either or both the 1979 EPA proposed water quality criteria and the FDA guidelines for edible freshwater species. All 71 reservoirs exhibited apparent problems with metals; because of data limitations, only 20 of the 71 showed potential problems with organic contaminants. The 71 potential problem reservoirs were distributed across all CE Divisions for which contaminants data were available. In addition, one or more toxic substances were reported to be a problem in an unspecified number of other CE reservoirs, though reliable quantitative data on the degree of contamination were lacking. Finally, Khalid et al. (1983) stated that comparisons of their results with those of previous surveys, including data from the Great Lakes, from EPA summaries for major US watersheds, and from a National Academy of Sciences study, "may suggest an underestimation of the magnitude of organic contaminant problems" in CE reservoirs.

17. Although Khalid et al. (1983) suggested that extensive contaminant problems potentially exist in CE reservoirs, these authors cautioned that the assembled data base was not sufficiently reliable or extensive to reach such a definitive conclusion. Indeed, perhaps the major finding of this preliminary survey was that the existing data base is inadequate to reach a reliable and defensible conclusion concerning the magnitude and extent of contaminant problems in CE reservoirs.

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Three general types of problems in the available data used by Khalid et al. (1983) can be identified.

18. The first general problem identified by Khalid et al. (1983) involved the manner in which water quality data are typically entered into available data base management systems, particularly the EPA STORET system. In most cases, results of whole-water (i.e., unfiltered) analyses are entered, whereas water quality criteria used for identification of contaminant problems are based on exposure to water-soluble concentrations of contaminants. Reported values often reflect only the prevailing lower limit of detection for a given contaminant rather than a true concentration value. Such limits of detection may change over time as analytical methods and instrumentation improve. Typically, the fact that an entered value is simply a lower detection limit is not recorded in the data base. Also, the analytical methods used to generate the recorded data are of unknown reliability and may have changed considerably over time. All of these problems together, especially the problem of reporting detection limits, may have combined to make reservoir contaminant problems appear more severe than they actually are.

19. A second general problem identified in the contaminant survey concerns the paucity of available data. Especially for organics, but also for metals other than iron, manganese, lead, and zinc, available data are insufficient to draw meaningful conclusions. For individual chemical contaminants, data on metals concentrations in water and tissues were located for a maximum of only 66 and 2 reservoirs, respectively. For individual organic contaminants, comparable figures for water and tissue concentrations were for a maximum of 11 and 10 reservoirs, respectively. Overall, data on only 109 out of over 500 CE reservoirs were located, and the frequency of reporting was uneven across Divisions (Khalid et al. 1983). One should not conclude from the results summarized earlier that those Divisions currently reporting more contaminants data have more severe contaminant problems. Moreover, conclusions concerning regional problems cannot be drawn from the data compiled by Khalid et al. (1983).

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20. The third problem identifiable in the results of Khalid et al. (1983) relates to the adequacy of existing contaminant monitoring programs. Most existing reservoir monitoring programs focus on classical water quality variables, with inadequate attention being given to chemical contaminants. Most Divisions and Districts surveyed exhibited a lack of adequate analytical capabilities and personnel trained for monitoring low-level contaminants. There was also a general lack of proper quality control in existing contaminant monitoring programs and a lack of clearly stated planning guidelines for monitoring contaminants. Finally, Khalid et al. emphasized the lack of a "quick-response" capability, the ability to monitor quickly and reliably the fate and impacts of an accidental toxic chemical spill into a reservoir.

21. Based on the material summarized in the preceding paragraphs, it is apparent that an adequate contaminant monitoring program is an essential first step in confronting potential reservoir contaminant problems. Carefully planned, well-executed, and statistically sound monitoring programs are required to: (a) determine if a contaminant problem exists in a given CE reservoir, and if so, the magnitude and extent of the problem; (b) document compliance with existing water quality criteria and standards; (c) develop reservoir management options for dealing with impacts of reservoir contaminant problems; and (d) verify that chosen management techniques are actually effective in reducing the severity of any existing contaminant problems. Partly in response to these needs, the OCE issued Engineer Technical Letter (ETL) 1110-2-281, "Reservoir Contaminants," dated 17 June 1983. This ETL provided guidance to all CE field operating activities on screening CE reservoir projects to ascertain the presence or absence of contaminants. Results of these screening activities are to be included in the annual Division Water Quality Reports. It is the intention of this report to provide assistance to CE Division and District personnel in responding to the requirements set forth in this ETL.

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Purpose and Scope

22. The purpose of this report is to provide general guidance to CE Division and District personnel on the design and conduct of programs for monitoring levels of chemical contaminants in reservoirs. The major issues to be considered in designing and carrying out a reservoir contaminant monitoring program will be discussed. It will not be possible to treat in a comprehensive manner every issue related to contaminant monitoring, or to provide specific guidance on the design of a blanket monitoring program applicable to all reservoirs and all contaminants. To be effective, monitoring programs must be both flexible and site specific. Flexibility implies that a monitoring program must be adapted to changes in management needs, to modifications of regulatory requirements, to improvements in analytical methodology and instrumentation, and to enhanced understanding of contaminant behavior in aquatic environments. Site specificity implies that the monitoring program is specifically tailored to the unique characteristics of a given reservoir and to the specific contaminant problems that are either known or suspected to occur there. Thus, it is imperative that the reader of this report adapt the general guidelines provided to his own unique circumstances, and that he continually evaluate the components of his monitoring effort for possible improvement.

23. The need for this report derives specifically from several conclusions of the initial survey of reservoir contaminant problems (Khalid et al. 1983): not all CE Divisions place the same emphasis on contaminant monitoring, the existing data base on contaminant levels in reservoirs is inadequate, and existing contaminant monitoring programs are often inadequate. In large measure, these deficiencies are a consequence of the relative newness of the concern with contaminants and of the fact that the presence of contaminants poses new problems for water resource managers not previously encountered with more conventional pollutants. As summarized in Table 1, these new problems are the result of several key differences between conventional and toxic pollutants. In contrast with conventional pollutants, toxic pollutants are more

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numerous, are typically synthetic rather than of natural origin, exist in the environment and exert an impact at low concentrations, may persist for long time periods strongly sorbed to suspended or bottom sediments, may strongly bioconcentrate, and may biodegrade to compounds of equal or greater toxicity. Because of these differences in properties, toxic contaminants pose unfamiliar sampling and analytical problems for which guidance is required.

24. This report is intended for use by all field personnel involved in designing, conducting, and analyzing the results of water quality monitoring programs in CE reservoirs. Guidelines provided here are intended to supplement existing information on general water quality monitoring programs. The focus is on expanding existing monitoring programs for traditional water quality constituents so that reliable and usable data on contaminant levels in reservoir waters, sediments, and biota are also collected.

25. Much of the information presented here is treated more thoroughly in other sources. This is especially true for the topics of sampling and analytical methods, statistical considerations, and the design of general water quality monitoring networks. For these, summary discussions of the relevant issues specifically related to contaminant monitoring will be provided, and the reader will be referred to the more definitive treatment elsewhere. Thus, this report provides general guidance on contaminant monitoring in reservoirs and serves as a guide to other, more extensive treatments of monitoring issues in key literature sources. In addition EM 1110-2-1201, "Reservoir Water Quality," provides guidance for the assessment of reservoir water quality conditions including reservoir releases and tailwaters. The EM emphasizes procedures to define program and/or study objectives and to select appropriate techniques for assessing water quality conditions in the planning, design, and water control management of reservoirs.

26. Information contained in this report is organized as follows: Part II presents the selection of the chemical contaminants to be monitored; Part III contains basic considerations concerning the design of monitoring programs; Parts IV and V summarize information on field

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sampling methods and analytical methods; Part VI summarizes guidance on the selection of contractors for conducting various portions of a monitoring program; Part VII summarizes issues concerning the management of data resulting from a reservoir contaminant monitoring program; and Part VIII considers the analysis and interpretation of contaminants data in relation to water quality criteria and standards and to management considerations. Proper use of this report assumes that the reader is familiar with the issues and problems discussed in the study of Khalid et al. (1983), which should also be considered prerequisite to this report.

PART II: SELECTION OF MONITORING VARIABLES

27. ETL 1110-2-281 provides guidance on the contaminants to be considered for possible inclusion in a monitoring program, and lists steps to be followed in screening specific projects for contaminant problems. If the screening process set forth in the referenced ETL reveals that inadequate data are available for reaching a management decision on the presence of contaminant problems, or that such problems do in fact exist, then field monitoring including sample collection and analysis may be required. In such cases, the identification of specific contaminant variables for inclusion in the monitoring program must be based on the best available information and screening procedures.

28. The selection of monitoring variables will depend in large measure on the anticipated uses of the resulting data. Inasmuch as data on contaminant levels in reservoirs will be used primarily to determine compliance with relevant water quality criteria and standards, it is the criteria and standards which define the potential sampling variables. Yet numerous chemical contaminants are covered by relevant criteria and standards, and it may not be necessary to sample all of these in a given reservoir. Conversely, other variables related to highly localized problems not covered by general water quality criteria may require monitoring. Thus, existing data and knowledge of contaminant loadings, concentrations, and environmental behavior must be taken into account in making the final selection of variables. As with the design of the overall monitoring program, the selection of monitoring variables must be both flexible and site specific, and must be continually reevaluated for effectiveness and relevance to management needs. Unnecessary sampling of contaminants wastes money and manpower and dilutes the effectiveness of the overall monitoring effort. Given the analytical costs and requirements for measuring contaminant concentrations in reservoir samples, the judicious selection of variables to be monitored is even more critical for a contaminant monitoring program than for the monitoring of more traditional water quality variables.

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29. The following sections discuss the selection of potential monitoring variables in relation to the criteria and standards summarized in Part I and the use of various screening procedures to further define the sampling variables. The specific environmental compartments (e.g., water, sediment) in which these variables are to be measured are treated in Parts III and IV of the report.

Potential Contaminant Monitoring Variables

30. In relation to the selection of potential monitoring variables, ETL 1110-2-281 defined a contaminant to be any water quality constituent that "(a) impairs project purposes, either legislated or actual; (b) violates State/Federal water quality standards; or (c) threatens humans, fish, or wildlife." This is clearly an extremely broad definition, encompassing conventional pollutants, heavy metals, organic toxicants, and other variables of localized interest.

31. Recognizing the need to restrict the operational definition of a contaminant, the referenced ETL further specified that, unless definite information exists that some other compound is of concern at a given project, the list of constituents to be considered for possible sampling should be limited to those on EPA's list of priority pollutants (excluding volatile organics), to chemicals covered by the EPA 1976 Red Book criteria, or to chemicals covered by applicable State or Federal criteria. This ETL also provided specific guidance on the inclusion of suspected carcinogens in contaminant monitoring programs and defined the concentration level of concern to be employed for carcinogens.

32. In relation to the specifications contained in the previous paragraph, Table 2 lists 77 chemical contaminants covered by the water quality criteria and standards summarized in Part I. This list was compiled based on information provided in the contaminants survey of Khalid et al. (1983). Contaminant concentrations specified to be of concern in these criteria and standards are tabulated in Khalid et al., in the original documents referenced by these authors, and in numerous other sources; they will not be repeated here. This list represents those

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chemical contaminants of prime regulatory concern in the Nation's waters. It consists of the so-called "List of 65" toxic pollutants covered by the 1980 EPA criteria (see Part I), plus several additional variables covered in the EPA 1976 Red Book criteria and in a variety of State water quality standards.

33. Similarly, Table 3 provides a list of 129 "priority pollutants." This list of 129 priority pollutants was published by the EPA and represents an expansion of the List of 65 previously published. The List of 65 includes a number of generic compounds (e.g., chlorinated benzenes, haloethers) comprised of several specific compounds each, so that it actually contains more than 65 individual toxic chemicals. Thus, all of the individual chemicals included in the priority pollutant list (Table 3) are also included in Table 2. Among the priority pollutants, the organics classified by Mills et al. (1982) as being volatile are also indicated in Table 3. Although ETL 1110-2-281 excludes volatile organic contaminants from consideration, all are covered by relevant State and Federal water quality standards and should be considered for possible inclusion in a monitoring effort. Table 3 also indicates the contaminants listed by Mills et al. (1982) as being the most frequently discharged into the Nation's waterways.

34. It is recommended that, at least initially, the chemical contaminants considered for possible monitoring be restricted to those shown in Tables 2 and 3. However, although this list provides a useful starting point in selecting contaminants for monitoring, it cannot be considered all-inclusive. It does not, for example, contain all variables likely to be of local or restricted interest (e.g., weathering products from specific geologic formations, saline inflows, compounds resulting from acid precipitation). More importantly, as new organic compounds are synthesized in industrial laboratories, as existing criteria are modified, and as improved understanding of contaminant behavior in aquatic environments reveals new chemicals of concern, this list of chemicals to be considered for possible inclusion in a monitoring program will need future modification. Again, Tables 2 and 3 represent a useful starting point for selecting monitoring variables, but the

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actual list of variables to be monitored at a given reservoir must remain flexible and site specific. The use of various screening techniques for selecting the variables from Tables 2 and 3 (and possibly others of local interest) for specific inclusion in a monitoring program at a specific reservoir is discussed in the next section.

Guidelines and Procedures for Contaminant Selection

35. In addition to providing guidance on the variables to be considered for potential inclusion in a reservoir contaminants monitoring program, ETL 1110-2-281 also discusses the steps to be followed in screening a reservoir project to determine the presence or absence of contaminant problems that might necessitate a field monitoring effort. The screening of a given reservoir was recognized as being an iterative process involving several key elements: assembly of existing information; careful evaluation of this information for quality, reliability, and timeliness; and the reaching of a decision that no problem exists, that additional information is required in order to reach a decision, that a contaminants problem exists requiring the implementation of a monitoring program, or that a reevaluation of the project is required at some specific future date.

36. The referenced ETL also considers various sources of data on reservoir contaminants, and discusses whether the decision that additional information is required before the presence/absence of a water quality problem can be ascertained would necessitate either the location of more difficult to obtain reports or information, or the initiation of a field sampling effort. Results of the initial survey of reservoir contaminants (Khalid et al. 1983) strongly suggest that the data base on contaminant levels in most reservoirs is presently inadequate and that the screening of reservoir projects in compliance with the referenced ETL will generally require at least some level of monitoring effort. Moreover, reservoir screening is an iterative process, requiring the continual scrutiny of existing data to determine whether further monitoring of the same or different variables is required.

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37. It is anticipated that as the screening guidelines and procedures are followed, the number of contaminants requiring detailed consideration will decline markedly. For example, consider a small reservoir located in an exclusively agricultural watershed for which existing data on metals concentrations indicate that no contamination problem exists. However, for this hypothetical reservoir, no data exist on synthetic organic compounds in the water, sediments, or biota. The selection of variables for possible inclusion in a monitoring program at this reservoir would focus on only those contaminants used within the watershed for agricultural purposes, most likely as herbicides or pesticides. In any case, the need exists to apply a set of scientifically sound, reliable, and easily used screening procedures to data on reservoir contaminants. Such screening methods should be capable of revealing whether a water quality problem exists in a given reservoir, and what chemical variables are of specific concern from a regulatory standpoint and should thus be included in the sampling effort.

38. Among the available screening methods are a set of scientifically sound, easily applied, and thoroughly documented techniques published by the EPA (Mills et al. 1982). These techniques grew out of an earlier set of methods developed for use in 208 planning studies for conventional pollutants (Zison, Haven, and Mills 1977). The revised and expanded techniques, consisting of a wide range of both empirical and mechanistic algorithms usable on desk-top calculators, are intended to yield a preliminary assessment of toxic pollutants in aquatic environments. Thus, these screening procedures are management tools useful for achieving water quality goals in reservoirs and other aquatic environments. The individual algorithms are based on those key processes (e.g., sorption, volatilization, photolysis) governing toxicant fate and transport in aquatic environments; these processes are analyzed in terms of first-order kinetics. The procedures are applied at several sequential levels of analysis, each successive level being characterized by fewer simplifying assumptions about the environmental behavior of the toxic chemical in question. Each level thus represents a successively more realistic "worst-case" scenario. The results derived at each level

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of analysis are compared with existing water quality criteria, the conclusion being reached that either a water quality problem is not anticipated (no further analysis required) or is likely (go to next level of analysis or recommend monitoring).

39. Thus, the primary goal of applying these screening procedures is to identify those water bodies where toxicants could reach hazardous levels as defined by relevant criteria. Careful and iterative application of these screening methods can therefore help in deciding whether monitoring is required in a specific reservoir, and what specific variables should be included in the monitoring program. For example, measurements or estimates of contaminant loadings to a given reservoir (e.g., derived from National Pollution Discharge Elimination System permit records) could be used with these techniques and the associated information on behavior and properties of toxicants summarized in the methods documentation (Mills et al. 1982) to predict whether any contaminants could reach hazardous concentrations. Careful application of these techniques could also suggest management options required for mitigating impacts of toxicants in reservoirs, or what additional information on toxicant fate and transport is needed in order to reach a reliable management decision.

40. Application of these screening procedures involves a number of steps, including assembly of the required data and information, identification of any problems obvious from an initial inspection of the existing information, determination of the variables to be screened, application of the methods, consideration of likely errors in the analysis, reevaluation of results, and formulation of recommendations (Mills et al. 1982). The consideration of possible errors is a critical aspect in the proper use of these methods. The environmental behavior of toxic chemicals is complex, whereas the screening methods are fairly simple and straightforward in their conceptualization and ignore many important processes in order to reach a quick answer. The user must be aware of likely sources of error and simplifying assumptions in evaluating results from a particular application. Proper scientific and engineering judgment must be exercised in using screening techniques such as these.

In many cases, the proper conclusion is that a more refined analysis is required.

41. To avoid redundancy, further consideration of the actual screening methods contained in Mills et al. (1982) is given in Part VIII of this report, as part of a general discussion of the interpretation of monitoring data. Several other similar screening approaches are also referenced there. The basic point to be emphasized here is that some type of screening procedure must be employed to decide whether a monitoring program is required for a given reservoir, as well as what specific chemicals, from the list of contaminants of possible interest (Tables 2 and 3), are to be sampled in such a program. The number of contaminants requiring monitoring at a specific reservoir will almost always be much smaller than the total list shown in Tables 2 and 3. Moreover, such screening procedures must be used continuously to evaluate the results and relevance of the current program design.

PART III: SAMPLING PROGRAM DESIGN

42. Once the decision has been reached to undertake a monitoring program at a specific reservoir for specific chemical contaminants, based on the general considerations outlined in Part II, it becomes necessary to specify the sampling objectives and to design the field sampling program. Water quality monitoring is a formidable and costly task, particularly for toxic contaminants. Its success depends on the development, documentation, and proper implementation of an appropriate sampling plan. If such a plan is well conceived and based on both rigorous statistical principles and information concerning the reservoir and contaminants in question, then the sampling program has the potential of yielding reliable and representative data which are interpretable in relation to monitoring program objectives. If this is not the case, and the sampling plan is poorly conceived or creates a source of error or bias in the resulting data, the purposes of the overall monitoring program will be compromised and the subsequent analysis of reservoir samples for contaminant concentrations, as well as the analysis and interpretation of analytical results, will be meaningless (Erlebach 1979, Langford 1979, Reckhow and Chapra 1983, Thornton et al. 1982, US EPA 1982).

43. Development of an appropriate sampling plan begins with the clear and careful specification of sampling objectives or purpose. To be useful, such objectives should be narrow and well defined, and should be operational in that they lead to the development of a specific sampling plan that will realize the stated objectives. The plan itself should follow directly from the sampling objectives, should be statistically sound, should be based on all available information on the reservoir and contaminants in question, and should lead to the collection of samples which are representative of the environment and the target or parent population(s) of interest. (Note that, in relation to sample program design, the term population is used here in the appropriate statistical sense rather than in the sense of a biological population. That is, the term "parent population" refers to the total universe of

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observations available for sampling, while the term "sample population" denotes the collection of observations which actually comprise the chosen sample. Inferences are drawn in relation to the parent population based on sampling statistics calculated from the sample population. Thus, the term population as used here may refer to actual or potential observations made on reservoir water, sediments, or biota.)

44. Because it is not possible to measure the entire population of interest, project objectives are realized by characterizing that population through sampling which is as accurate and precise as possible. subject to project constraints of cost, time, and manpower. Thus, the chosen sampling design must balance sampling costs against the reliability or uncertainty inherent in the resulting data, thereby minimizing (subject to project constraints) uncertainty in monitoring data or partitioning that uncertainty or variability into interpretable and meaningful components. Various pilot or reconnaissance efforts, perhaps involving remote sensing, may be undertaken prior to selecting the final sampling design (Erlebach 1979, Langford 1979, Reckhow and Chapra 1983, Rice and Anderson 1979, Thornton et al. 1982, US EPA 1982).

45. As with all other components of the monitoring program, the sampling plan selected should be both site specific and flexible. This plan must reflect the application of the general criteria discussed here to the reservoir under study through the use of all site-specific information available to the project manager. A number of factors must be considered in developing a site-specific sampling plan, including the following: contaminant properties and environmental behavior; watershed and basin characteristics; hydrologic, climatologic, and geochemical characteristics of the reservoir and the surrounding watershed; inpool hydrodynamics and general water quality dynamics; reservoir morphometry; and project purposes and operation. Flexibility simply implies that the sampling plan may be modified over time as new information and data accumulate and as sampling purposes or objectives change.

46. In the paragraphs which follow, factors that should be considered in designing a flexible, reservoir-specific sampling plan are reviewed. The first section below discusses a number of general issues

related to sampling plan design, while the second summarizes basic statistical principles underlying sampling. Subsequently, reservoir-specific factors which influence the determination of sample size, the selection of specific sampling locations, and the choice of sampling frequency are discussed. Implementation of the chosen sampling design is considered in Part IV.

47. The design of water quality monitoring programs is discussed in a number of other useful references. Gaugush et al. (1984) and EM 1110-2-1201 both provide extensive discussions of the design on monitoring and intensive sampling programs for reservoir water quality studies. Other sources, including Reckhow (1979a, 1979b), Reckhow and Chapra (1983), and US EPA (1982), discuss sampling design in a general water quality context. Both the American Chemical Society (ACS) (1980) and Kratochvil and Taylor (1981) discuss sampling design in relation to the analysis of environmental samples for contaminant concentrations. Basic references on statistical sampling theory include Cochran (1963) and most of the statistics texts cited in Parts VII and VIII of this report. These references should be consulted for further details concerning sampling program design.

General Sampling Considerations

48. This section discusses a number of general issues which should be considered in designing field sampling efforts as part of a reservoir contaminant monitoring program. These factors include existing knowledge of (a) water quality conditions in the study reservoir, (b) general contaminant problems in reservoirs, and (c) contaminant behavior in aquatic environments, as well as the specification of detailed sampling objectives, the decision as to which environmental compartments to sample, and the development and documentation of the resulting sampling plan.

**Relation to ongoing water
quality monitoring programs**

49. Existing data on water quality conditions in the study reservoir should be invaluable in designing a sampling plan for contaminants in that reservoir. Such data will provide information on when, where, and how to sample for contaminant concentrations, and may provide general information on the major physical, chemical, and biological processes that determine the behavior of both conventional and toxic pollutants in the study reservoir. Moreover, it may be possible to combine contaminant sampling with ongoing sampling programs for conventional water quality constituents. This will not only provide important ancillary information which will prove useful in interpreting results of contaminant sampling, but may also reduce sampling costs and manpower requirements for a new and separate contaminant monitoring effort.

50. The project manager should not feel compelled to combine contaminant sampling with ongoing water quality sampling programs if this would compromise the stated sampling objectives. Because the existing data base on reservoir contaminants is so sparse, and because the environmental behavior of toxic pollutants differs in many ways from that of more conventional pollutants, it may be necessary to design a new and largely separate sampling effort for reservoir contaminants. Thus, to the extent that combining contaminant sampling with ongoing water quality monitoring reduces sampling costs and provides useful ancillary data, it should be encouraged. But, to the extent that it compromises basic objectives of the contaminant monitoring effort, it should be avoided.

**Knowledge of existing
reservoir contaminant problems**

51. Information on existing contaminant problems in CE reservoirs, as summarized by Khalid et al. (1983), should also be useful in designing a sampling program for contaminants in a specific reservoir, whether that specific reservoir was included in the Khalid et al. survey or not. Results of this survey provide important information on the nature and sources of contaminant problems in reservoirs, on the

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existence of data bases on reservoir contaminants as well as problems to avoid in entering new data or retrieving data from these data bases, and on the proper analysis and interpretation of the results of contaminant monitoring programs. Although many of these issues are treated in detail in this report, information on existing reservoir contaminant programs contained in the earlier report of Khalid et al. should be considered carefully by anyone undertaking the design of a sampling program for reservoir contaminants.

Knowledge of contaminant
behavior in aquatic environments

52. Also essential to the design of an acceptable sampling plan for reservoir contaminants is information on those factors which regulate the environmental behavior of toxic pollutants in aquatic environments. Because the physicochemical and biological environment of reservoirs (and streams) is so different from that of pollutant sources, one must have a thorough general understanding of those factors which regulate contaminant persistence and availability in order to design a proper sampling plan (Khalid et al. 1983). In particular, one must understand the possible sources of contaminants to reservoirs, as well as the physical, chemical, and biological factors which regulate not only contaminant transport, dispersion, and partitioning in reservoirs, but also their uptake, accumulation, and effects in aquatic food chains. Especially critical for organic contaminants is an understanding of sediment dynamics in reservoirs.

53. Both Khalid et al. (1983) and Mills et al. (1982) summarize extensive information on contaminant behavior in reservoirs (and other aquatic environments), on contaminant properties which regulate their environmental behavior, and on contaminant sources to aquatic environments. The latter reference also contains screening procedures that are useful in deciding what transport and transformation processes are most important in regulating the environmental dynamics of specific contaminants. Other useful sources of information on contaminant sources, properties, and environmental behavior include Callahan et al. (1979);

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Lyman, Reehl, and Rosenblatt (1982); Stumm and Morgan (1981); Tinsley (1979); and Verschueren (1983).

Specification of sampling objectives

54. As indicated above, sampling program design begins with the clear and concise statement of sampling objectives, which are narrow, well defined, and operational. Because monitoring for its own sake is costly and results in data of dubious quality and utility, sampling objectives must be carefully and thoroughly specified at the outset and the sampling program designed specifically to realize these objectives. Failure to define sampling objectives carefully will compromise the success of the entire sampling effort. Conversely, proper specification of objectives facilitates the design of an effective and statistically efficient sampling program which balances sampling costs against data uncertainty/reliability, and enhances the value of sample collection and analysis for realizing the stated objectives.

55. The sampling objectives should specify the target population(s) about which information is desired (i.e., the real population about which inferences are to be made), the specific measures or observations to be made on this population, the variables or parameters to be measured (e.g., the contaminants to be analyzed), the problem to be solved (i.e., the decision to be reached or the goal to be achieved), and how the analysis and interpretation of sampling results relate specifically to the resolution of this problem (Gaugush et al. 1984, Langford 1979, Rice and Anderson 1979, Sanders and Ward 1979).

56. In relation to reservoir contaminant problems, many different sampling objectives may be envisioned, each leading to a different sampling design. Moreover, sampling objectives may evolve over time, as data accumulate, as "old" problems are resolved, or as "new" problems are discovered. Thus, sampling program design may change over time, often substantially.

57. In some cases, sampling objectives may involve determining whether or not a given reservoir is in compliance with existing water quality criteria and standards (i.e., do measured concentrations of certain contaminants exceed specified standards?). For such a general

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objective, existing data may be quite sparse and field sampling may
involve a fairly coarse sample collection network in space and time. In
other cases, sampling objectives might involve the detection of temporal
trends in contaminant concentrations, requiring a more fine-scale sam-
pling network and more extensive background data. Similarly, sampling
objectives could involve determining whether some specific reservoir
management procedure had led to the mitigation of a previously detected
contaminant problem. As with the previous case, such an objective might
require a more restricted sampling network in spatial terms, and would
be based on a much more extensive background data set.

58. Another type of study objective is one that specifies the
conduct of a number of ancillary, intensive studies on the processes
that regulate contaminant behavior in the study reservoir, with the hope
of identifying a specific management option for mitigating a known con-
taminant problem. Similarly, specified objectives could call for the
collection of considerable ancillary data on traditional water quality
variables, to assist in the interpretation of contaminant monitoring
results.

59. These hypothetical objectives obviously are not as detailed
or specific as those for an actual sampling program design. They are
included to emphasize the fact that many different objectives are pos-
sible in reservoir contaminant monitoring programs.

Environmental
compartments to be sampled

60. One of the major decisions to be made in finalizing the sam-
pling plan for a contaminant monitoring program concerns the specific
environmental compartment(s) to be sampled--i.e., water, sediment, or
biota. Although most of the relevant water quality criteria and stan-
dards reviewed in Parts I and II specify critical water-soluble concen-
trations that are not to be exceeded in aquatic environments, the direct
collection and analysis of samples of reservoir water for contaminant
concentrations may not always be the most desirable sampling strategy.
This is especially true if water concentrations are quite low, near
analytical detection limits, and also highly variable in space and/or

time. In such cases, the collection and analysis of sediment or biological tissue samples may be more useful in detecting contaminant problems in the study reservoir.

61. Deciding which compartments to sample in a specific reservoir requires general understanding of the major factors regulating the environmental behavior of specific contaminants in aquatic environments (see paragraphs 52-53 above). Specific chemical contaminants may be degraded chemically or biologically under certain environmental conditions; they may also change form due to the action of a variety of biogeochemical processes. Because of the action of these processes, certain contaminants may accumulate in sediments and/or bioaccumulate in aquatic food chains. Such contaminants may persist in reservoirs for long time periods, especially in sediments, if they are particularly resistant to degradation and strongly sorbed to organic matter. The degradation products of contaminants may also persist and be toxic (Khalid et al. 1983, Mills et al. 1982). Understanding such relationships is critical to selecting the proper environmental compartments to sample in a given monitoring program in order to realize stated sampling objectives. Some of the general issues to be considered in deciding whether to sample reservoir water, sediments, or biota are reviewed in the next three paragraphs.

62. **Water.** Because (a) most water quality criteria and standards specify water-soluble contaminant concentrations not to be exceeded, and (b) most monitoring programs will have as their major objective the determination of compliance with these criteria and standards (i.e., is the reservoir in compliance or in violation?), most sampling programs for reservoir contaminants will focus on the collection and analysis of water samples from appropriate sampling locations, at times specified in the sampling plan.

63. Indeed, the majority of monitoring programs in this country focus on water sampling; most existing sampling and analytical protocols are similarly based on water sampling. In the majority of cases, as long as water samples are properly filtered so that the resulting data correspond to the form of the contaminant specified in the relevant

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criteria and standards, this is an acceptable and useful approach. However, under the more difficult sampling conditions (paragraph 60), the collection and analysis of water samples alone may provide data of great uncertainty that are not useful for detecting the presence of reservoir contaminant problems. Moreover, collection of only water samples provides almost no information on the factors regulating the environmental behavior of the contaminants in question in the study reservoir.

64. **Sediments**. Particularly because the dynamics of many toxic pollutants, especially organic contaminants, are so closely tied to the dynamics of sediments within reservoirs, the determination of contaminant concentrations in sediment samples may be an especially important component of a reservoir monitoring program. Major inputs of contaminants to reservoirs may occur in association with sediment transport, with contaminants often being lost from the water column due to subsequent sediment deposition. Contaminants may also be released to the water column at slow rates over long time periods due to diffusion out of contaminated bottom sediments, or to the resuspension of bottom sediments and the desorption of adsorbed contaminants. Thus, sediments may serve both as short-term sinks and as long-term sources of contaminants; in the latter case, this may be true long after inputs of contaminants to the reservoir have been eliminated (Khalid et al. 1983, Mills et al. 1982, US Geological Survey (USGS) 1977).

65. Collection and analysis of both suspended and bottom sediment samples may reveal not only the existence of contaminant problems in the sampled reservoir, but also what processes are critical to the regulation of contaminant concentrations in the water column and in aquatic biota. Also, the collection, careful vertical sectioning, and laboratory analysis of sediment cores may provide important information on the contamination history of a specific reservoir.

66. **Biota**. Because biological organisms are capable of accumulating contaminants present at low environmental concentrations to potentially toxic levels within their bodies, they may be especially valuable components of a contaminant sampling plan. In particular, they may prove to be especially sensitive indicators of the presence of

contaminant problems in the study reservoir, even if the occurrence of such problems is not detectable from water or sediment sampling (Erlebach 1979, Khalid et al. 1983). Organisms may take up and bioconcentrate contaminants from water or sediments (bottom or suspended). Uptake may occur through the ingestion of contaminated food or sediment; from water through absorption across gill surfaces, adsorption to the outer body surface (e.g., by phytoplankton), or cuticular diffusion; or via direct absorption from sediments. The degree to which contaminants are concentrated by organisms is related primarily to the lipid content of the organism, the water solubility of the contaminant, and the duration of contact between organism and contaminant source.

67. Because various animal species are especially mobile (e.g., fish) or live in intimate contact with sediments (e.g., benthic organisms such as oligochaetes), they may be especially valuable components of a sampling program to detect the presence of reservoir contaminant problems. Aquatic macrophytes and phytoplankton may also be important candidates for sampling, depending on the environmental conditions and contaminants involved. The sampling plan must specify what particular species are to be sampled, as well as (under some circumstances) what life stages and body tissues are to be collected and analyzed.

Development of sampling plan

68. Once the sampling design has been finalized, it should be carefully documented in a detailed, written sampling plan (ACS 1980, Erlebach 1979, Plumb 1981, US EPA 1982). The final plan should have been agreed upon by all program participants, and should be circulated to these same individuals for their reference and retention. Development of the final plan may have required the conduct of pilot or reconnaissance studies, perhaps in association with ongoing water quality surveys of the reservoir in question. Preparation of a written sampling plan is essential to the success of reservoir contaminant monitoring programs, especially those programs of long duration. The sampling plan should be flexible, allowing for the incorporation of design changes or

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improvements based on field experience or sampling results. It should also be updated as sampling objectives or design evolves.

69. All aspects of the sampling program should be thoroughly described in the sampling plan. Specific factors to be included are: the detailed sampling objectives, including definition of the target population(s) of interest, the observations to be made on this population, the variables to be measured, the problem to be solved, and the relation of data analysis and interpretation to problem resolution; details of sample size, replication, location, and frequency; discussion (if appropriate) of statistical considerations underlying the specified sample design; specification of field sampling methods and apparatus, as well as methods of sample treatment and processing; desired level of precision/acceptable error level in study results; appropriate confidence levels for subsequent statistical analyses of sampling data; and all other information required for the documentation and successful implementation of the chosen sampling design. The detailed sampling plan is one component of the quality assurance plan for the overall monitoring program, which includes other elements as specified in Part IV.

Statistical Considerations in Sampling

70. In addition to the general sampling considerations discussed in the previous paragraphs, the design of sampling programs for reservoir contaminants must be based on the rigorous application of sound statistical principles. In some cases, the paucity of background data on contaminants in reservoir waters, sediments, and biota may make it difficult to determine the appropriate sampling size and frequency (ACS 1980, Reckhow 1979b). Moreover, for contaminant monitoring programs, sample size and frequency may be more strictly regulated by available project resources than by other, more traditional sampling considerations (Plumb 1981). Nonetheless, the application of statistical principles, perhaps combined with the conduct of short-term pilot studies, can still lead to the design of efficient and effective sampling programs for reservoir contaminants, and to considerable savings in

time, manpower, and money (Kratochvil and Taylor 1981; Reckhow 1979a, 1979b).

71. Application of rigorous statistical principles to the design of contaminant monitoring programs forces one to consider explicitly those factors which determine the final experimental design, and to examine the specific trade-offs inherent in the chosen design between the costs of sampling and the uncertainty in the resulting data (Reckhow 1979a, Reckhow and Chapra 1983, Thornton et al. 1982). Too often water quality monitoring programs are designed based solely on issues of sampling convenience in space and time. Although such programs may be relatively easy to implement and inexpensive, they may also generate data having little utility in relation to stated project purposes. To be effective, sampling must reflect both the cost of sampling and the variance or uncertainty inherent in the populations being sampled.

72. Equations arising from statistical sampling theory, summarized below, allow one to do this explicitly. In these equations, sampling convenience may enter in relative to the cost of sampling. But it must be balanced against the uncertainty and, hence, utility of the resulting data for realizing stated sampling objectives. Proper application of the statistical equations summarized here, based on sound scientific and engineering judgment, will not only lead to the design of an efficient sampling plan, but also to the definition of data needs in relation to sampling objectives and to the explicit quantification of uncertainty in the resulting population estimates. Moreover, sample design based on statistical principles will explain or eliminate as much variability as possible through the selection of sampling variables, locations, and times, subject to project constraints of cost, time, and manpower.

Sample size and allocation

73. The first set of decisions to be made in the rigorous design of sampling programs for contaminants concerns the specification of sample size as well as (where appropriate) the allocation of total sampling effort among discrete sampling strata. These decisions, in turn, require user-supplied information on the desired level of precision (or

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its converse, error) in sampling results, the cost of sampling, and the variability inherent in the populations being sampled. Relevant statistical formulas for making these decisions are summarized in Table 4 and are discussed in the following paragraphs in relation to several types of random and nonrandom sampling programs.

74. _Simple random sampling_. Simple random sampling involves the random selection of sample locations in such a manner that every potential sampling site has an equal probability of being included in the chosen sample population. Sample locations are frequently selected with the use of random number tables. The key assumption involved in the design of such a sampling program is that all sampling units are essentially homogeneous with respect to the variables of interest. Thus, this type of sampling approach would be employed if there was no reason to subdivide the total reservoir into subareas or strata for sampling purposes. In other words, this type of sampling approach would be applicable only to unstratified reservoirs that do not exhibit strong longitudinal or lateral gradients in contaminant concentrations or other relevant properties.

75. Equations 1 and 2 in Table 4 provide a means of estimating sample size and cost for a random sampling program to achieve a specified level of precision in sample data, given the amount of variability in the population being sampled. These two equations may be solved iteratively in order to match sample size and desired precision with available project resources. Also, Equation 1 (and similar equations for the case of stratified random sampling) must be solved in iterative fashion in order to match the calculated sample size with the proper value chosen from the Student's t distribution. Initially, a value of $t = 2.0$ may be chosen, corresponding to a 95-percent confidence level and $n > 30$. Then, the equation is resolved, with appropriately selected values of t corresponding to the most recently calculated sample size, until convergence is achieved (see Thornton et al. (1982) for examples). Where the sampling program involves a number of different contaminants, one should choose the largest calculated value of the sample size in

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order to achieve the desired level of precision for all sampling variables.

76. Use of these equations (and others in Table 4) requires that an estimate of the sample variance be available for each of the monitoring variables of interest. Such estimates may be (a) provided by existing data on the population to be sampled or on a similar population, (b) based on informed judgment, or (c) based on the conduct of an appropriate pilot study. Where preliminary estimates of variances are used, it may be necessary to redefine sample size later as more reliable data become available (Cochran 1963, Reckhow and Chapra 1983).

77. Stratified random sampling. Stratified random sampling involves partitioning the total reservoir into discrete subareas or strata for sampling purposes. Within each stratum, sampling is conducted randomly. Each stratum is assumed to be relatively homogeneous but to differ in relevant characteristics from other chosen strata. In other words, strata are defined such that within-stratum variances are minimized whereas between-stratum variances are maximized. Such a sampling design requires data on variances of contaminant variables of interest within the study reservoir; this information again may result from a properly designed pilot study. Typically, stratification produces a more efficient sampling plan and reduces the total sample size required to achieve a desired level of precision in estimated population parameters, as compared with simple random sampling. It would be the sample design of choice in a density-stratified reservoir or one exhibiting pronounced lateral or longitudinal gradients in contaminant concentrations or other relevant properties (i.e., most existing reservoirs). In general, the gains in sampling efficiency are diminished after a few (three to five) strata are defined (Reckhow and Chapra 1983, Thornton et al. 1982, US EPA 1982).

78. Table 5 presents equations for calculating total sample size and cost, as well as allocation of sampling effort among chosen strata, for three types of stratified random sampling designs.

> a. In equal allocation, an equal number of samples are collected from each chosen stratum (Equations 4-5). No

stratum is weighted more heavily than another (e.g., due to differences in size among strata), and sampling costs are assumed to be roughly equivalent across all strata.

b. Proportional sample allocation involves distributing total sampling effort among strata according to user-selected weighting factors (Equations 6-7). These factors typically represent the fraction of total reservoir surface area or volume (or some other measure of relative size) which is accounted for by a given stratum. Thus, in this approach, those strata that are larger or which exhibit greater variability in relevant population parameters receive greater sampling effort. Again, however, sampling costs are assumed to be effectively constant for all strata.

c. In the last case considered, optimal allocation, sampling effort is allocated among strata based on differences in sample variability, stratum size, and sample costs (Equations 8-10). Hence, those strata that are larger, or which exhibit greater sample variability, or which are less costly to sample, receive a greater fraction of the total sampling effort. Two separate equations are given for total sample size, depending on whether precision or cost is assumed to be fixed at the outset. Equation 8 will lead to the estimation of the population parameters of interest to a user-specified level of precision at minimum cost. In contrast, Equation 9 will minimize the uncertainty present in the estimates of the population parameters of interest, subject to a user-specified cost constraint. In general, the iterative solution of Equations 3 and 8, such that a matching of desired precision and resultant costs is achieved, would seem to be a more desirable approach to specifying total sample size for optimal allocation of sampling effort in contaminant monitoring programs than would the solution of Equation 9.

79. <u>Systematic random sampling</u>. This type of sampling design is frequently employed in reservoir water quality studies. It involves regular sampling in space, once the initial sampling location is selected randomly. Frequently, sampling sites are located with reference to a regularly spaced grid, which is superimposed on a map of the study reservoir. A systematic random sampling design is often easier to implement than a truly random design, and it may prove to be an effective means of sampling over the entire reservoir surface and of uncovering heterogeneities that might be missed in a random sample. It may also be a useful design for initial pilot studies prior to selecting the

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final sampling design (Gaugush et al. 1984, US EPA 1982).

80. Although most statistical analyses of sample data assume that such data have resulted from a strictly random sample, these same analyses may still be performed on data generated by a systematic random sampling design, especially if the initialization point is chosen in a truly random manner. In particular, random sampling equations, both for sampling program design (Table 4) and for final data analysis, may be employed for systematic random sampling if no bias is introduced by the sampling design itself, if the population being sampled does not undergo periodic variation, or if such variation is unrelated to (not confounded with) the location of sampling points (Reckhow and Chapra 1983). Where these conditions are met, Equations 1 and 2 shown in Table 4 for a simple random sampling design may be employed to determine sample size and cost for a systematic random sampling design.

81. Nonrandom sampling. In general, because it complicates the analysis and interpretation of sample data, a nonrandom sampling design should not be used as part of a reservoir contaminant monitoring program. Such a design should be employed only if specifically justified in relation to the reservoir or variables of interest or to sampling objectives (US EPA 1982). For example, it might be a useful design to determine whether a specific reservoir management strategy resulted in the reduction of contaminant concentrations in a given fish population located in a specific region of the sampled reservoir.

Sampling frequency

82. The second major decision to be made in sampling program design for reservoir contaminant monitoring concerns specifying the times at which samples should be collected, i.e., determining the sampling frequency. In a very real sense, rigorous specification of sampling frequency is an identical problem to the specification of sample size and allocation as discussed in the paragraphs above.

83. Determining sampling frequency involves specifying the location of sampling points in time, just as determining sample size and allocation involves specifying the location of sampling points in space. Thus, based on the same equations as summarized in Table 4, one may

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specify sampling frequency in a simple, stratified, or systematic random
fashion. In this case, however, one is interested in deriving estimates
of population variance over time at a specific location, rather than
variance of population properties in space, as was the case above.
Using this approach, one may specify different sampling frequencies at
different sample locations, if such an approach is justified by existing
data and study objectives. Such an approach, however, may lead to
practical problems in implementation.

84. The case is made below (paragraph 105) that specification of
sampling frequency in a stratified random fashion is preferable to
either simple or systematic random sampling in time. In such a case,
the total sample period (e.g., 1 year) is stratified into meaningful and
essentially homogeneous periods based on knowledge of those processes
(e.g., hydrologic events, biological growth) regulating contaminant
behavior in the sampled reservoir.

85. One major differences does exist in the specification of sam-
pling frequency as compared with the determination of sample size and
allocation. Statistical formulas summarized in Table 4 assume that
individual sample values used to calculate the required sample variances
are statistically independent (i.e., uncorrelated). However, most real
time series of environmental variables of interest show a high degree of
serial autocorrelation, i.e., individual sample observations are corre-
lated over time and, hence, are not statistically independent. In most
practical cases relevant to the design of contaminant monitoring pro-
grams, this lack of strict statistical independence does not represent
an overly severe violation of the assumptions underlying the equations
summarized in Table 4, which may be used to specify appropriate sampling
frequencies.

86. In cases where the degree of serial autocorrelation in rele-
vant water quality time series is felt to be sufficiently large to war-
rant a more sophisticated approach to determining sampling frequency,
perhaps based on time series analyses which take explicit account of the
autocorrelation structure of existing data, the reader is referred
specifically to Loftis and Ward (1979), as well as to the general

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discussions found in Box and Jenkins (1976) and Gaugush et al. (1984).
Another useful reference is the paper of Casey, Nemetz, and Uyeno
(1983), who derive statistical measures of the effectiveness of
specified sampling frequencies for detecting water quality violations.

Factors Influencing Number of Samples

87. Discussions in the previous paragraphs summarize basic sta-
tistical principles upon which sampling design should be based for con-
taminant monitoring programs. Application of these principles in a
given monitoring program requires a variety of reservoir- and
contaminant-specific information in order to calculate the desired
quantities listed in Table 4. The types of program-specific factors
which need to be considered in determining total sample size are
reviewed in this section.

Cost and manpower requirements

88. Because the determination of contaminant concentrations in
environmental samples is such a difficult task, requiring the careful
application of proper and often highly sophisticated procedures of sam-
ple collection, handling, and chemical analysis, sample size may be more
closely related to cost and manpower requirements than to any other sin-
gle factor (Plumb 1981). This is especially true if numerous organic
contaminants are to be analyzed as part of the monitoring effort. This
statement does not imply that precision of sampling results is a less
important consideration. Indeed, as emphasized earlier, sampling design
seeks to balance sample cost against resulting data uncertainty. But,
it does emphasize that the resources required to process environmental
samples for contaminant analyses will be a prime determinant of the num-
ber of samples to be collected in a reservoir monitoring program.

89. In order to determine the relationship between sample size
and resources required to process this sample load, estimates of the
cost and manpower requirements for each step in the monitoring program,
from sample collection through laboratory analysis and data reduction,
must be available. In relation to this need, Plumb (1981) provides

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estimates of the analytical costs, manpower requirements, and approximate maximum daily sample loads for the laboratory analysis of a wide variety of traditional and toxic pollutants. Similarly, the EPA has published (Federal Register, 1979, Vol 44, pp 75028-75052) cost estimates for the implementation of their recommended procedures for the analysis of organic priority pollutants (Longbottom and Lichtenberg 1982). These and other available cost estimates can be used with the proper equations from Table 4 to match sample size against available project resources.

Precision of concentration estimates

90. The user-specified level of precision in sample results is a second factor that influences sample size. Although a high degree of precision in monitoring data is a desirable goal, which increases confidence in study results, the specification of precision in the final sampling plan must be balanced against both project resources (i.e., cost) and population variability. Where variability in the population(s) of interest is relatively low, a high degree of precision may be achieved without collecting more samples than can be accommodated by the authorized project budget. Conversely, if population variability is quite high, a lower level of precision may have to be accepted if total costs are to remain within the project budget.

91. The specified level of precision (and hence sample size) is also related to study objectives. For example, if the major study objective is the initial determination of the presence or absence of contaminant problems in the study reservoir, then a somewhat lower level of precision (and hence a smaller sample size) may be acceptable. However, if the objective is to determine whether a specific reservoir management strategy has resulted in the reduction of a known contaminant problem (e.g., a reduction of polychlorinated biphenyl (PCB) levels in a reservoir fishery), then a higher level of precision (and a concomitantly larger sample size) may be required. Thus, the influence of precision on sample size must be considered carefully in relation to sampling objectives, inherent variability in the target populations of interest, and available project resources (Reckhow and Chapra 1983).

Reservoir age,
morphometry, and operation

92. The interrelated factors of reservoir age, morphometry, and operation influence the choice of an appropriate sample size. These factors affect the spatial heterogeneities in the distribution of contaminant concentrations and other relevant water quality characteristics in the reservoir. Where such heterogeneities are pronounced, a larger sample size will be required in order to achieve the desired level of precision. Conversely, where such heterogeneities are less pronounced, a smaller sample size is acceptable.

93. Among these three factors, morphometry is clearly the most important. Complex, sinuous, highly dendritic reservoirs having large littoral zones as well as numerous coves and embayments present severe sampling challenges and require larger sample sizes than do less complex reservoirs. Interactions between morphometry and inflows, which may be confined largely to a zone of conveyance along the old river channel, can increase spatial heterogeneities, especially through in-pool hydrodynamics and mixing processes (Ford and Johnson 1983). Location of various project features such as bridges, which alter circulation patterns, can similarly influence the presence of spatial heterogeneities and hence sample size.

94. Age is important in relation both to the development and spatial differentiation of aquatic sediments as regulated by in-pool circulation patterns, and to the establishment and habitat differentiation of biological populations within reservoirs. Reservoir operation, especially the timing, magnitude, and vertical placement of project releases, can also contribute to spatial heterogeneities, largely through effects on in-pool hydrodynamics and mixing processes. These and other sources of heterogeneity increase the population variances of interest and thus the required sample size, and should be carefully considered in finalizing the sample plan.

Occurrence of spatial gradients

95. Vertical, longitudinal, and lateral gradients in contaminant concentrations and other water quality variables represent special cases

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of spatial heterogeneity which must be evaluated fully in relation to sample size determination. The presence of vertical stratification, produced by the interaction of surface energy exchange and mixing processes with the depth and inertia of the impounded water, can exert a profound influence on contaminant behavior in the study reservoir. Longitudinal gradients may also be quite important in many reservoirs, providing another source of spatial heterogeneity in contaminant distribution. These gradients largely result from the fact that most reservoirs are larger, deeper, and morphometrically more complex than natural lakes, with a single large inflow located a considerable distance from the outflows (Thornton et al. 1982).

96. The interaction of inflow placement and mixing with this morphological pattern typically results in profound changes in water quality conditions and sedimentation patterns along the longitudinal axis of the reservoir (Thornton et al. 1981). Lateral gradients may also influence the dynamics and distribution of reservoir contaminants. Such patterns result from the restriction of inflows to a zone of conveyance along the old river channel and from the presence of large, shallow littoral zones around the reservoir margin. All of these sources of spatial heterogeneity must be evaluated when determining sample size using the statistical formulas in Table 4.

Factors Influencing Selection of Sampling Locations

97. In those circumstances in which a reservoir contaminant monitoring program is to be based on either a simple or a systematic random sampling design, the detailed consideration of site-specific information in locating sampling points in space will be relatively unimportant. Those reservoirs for which such a sampling design is chosen will tend to be relatively small, shallow, and homogeneous. In these cases, sample location will typically be determined with the aid of a random number table (simple random sampling) or by superimposing a regularly spaced grid over a topographic or other map of the reservoir (systematic random sampling). However, for larger, more complex reservoirs which exhibit

pronounced spatial gradients and heterogeneities (the majority of CE reservoirs), a stratified random sampling design will be most appropriate. In these cases, specification of sampling locations will involve defining relatively homogeneous sampling strata based on all relevant site-specific information, and allocating total sampling effort among the chosen strata. The actual location of sampling points within the defined strata should be done in a random fashion (simple or systematic). The major factors to consider in defining discrete sampling strata for contaminant monitoring programs in reservoirs are discussed in the following paragraphs.

Cost and manpower requirements

98. Although one cannot simply choose sampling sites based solely on convenience, neither can one ignore the effects of site accessibility or ease and cost of sampling on the specification of sampling locations. Sampling sites should be randomly selected and representative of the stratum within which they occur. However, the location of a large number of sampling sites in areas of poor accessibility, or in areas where sample collection is difficult and time consuming, will reduce the total number of sites that can be reliably sampled in a reasonable time frame, and perhaps lead to reductions in the reliability and precision of overall monitoring results. Thus, the effects of sample site location, accessibility, and ease/cost of sampling must be evaluated carefully in relation to study objectives, project resources, and data reliability. Sampling convenience should not be the major factor used in selecting sampling locations, but its influence on sampling costs and manpower requirements must be considered in relation to project funds and other available resources.

Reservoir age,
morphometry, and operation

99. As indicated above, these interrelated factors are responsible for the presence of spatial heterogeneities in the distribution of contaminants and other water quality constituents of interest in the sampled reservoir. These heterogeneities include spatial variability in dissolved contaminant concentrations and in physical and chemical

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properties of bottom sediments, as well as specific habitat associations of biological populations of reservoirs. Thus, such heterogeneities should provide the basis for the definition of sampling strata within the study reservoir in a manner consistent with stated sampling objectives. For example, coves and other near-shore littoral sites would be placed into a different sampling stratum than would sites in the main pool of the impoundment near the dam. Such strata would differ in many relevant properties which influence contaminant behavior, including sediment characteristics, resident biological populations, and hydrodynamics and mixing processes, and should thus be sampled differentially.

100. Major tributaries which drain watersheds having dissimilar land-use patterns (e.g., predominantly forested versus predominantly agricultural) would also be a basis for stratum definition, as would the location of project features that alter water circulation patterns and create zones of relatively turbulent or quiescent water. Stratified random sampling designs include consideration of spatial heterogeneities in order to produce an efficient sampling plan that minimizes sampling cost while maximizing data reliability in relation to sampling objectives and available project resources.

Occurrence of spatial gradients

101. Gradients—along the vertical, longitudinal, and lateral reservoir axes—represent special types of spatial heterogeneity which profoundly alter the behavior of contaminants in reservoirs and thus require careful evaluation in relation to the definition of sampling strata (Gaugush et al. 1984, Khalid et al. 1983, Mills et al. 1982, Plumb 1981, USGS 1977). Vertical gradients (i.e., density stratification) are extremely important in relation to contaminant behavior in reservoirs. Where stratification is absent, the reservoir is fully mixed, and hypolimnetic anoxia is not present. However, in stratified reservoirs, vertical mixing is inhibited, density currents are prevalent, hypolimnetic reaeration is reduced, and bottom anoxia is likely to occur. All of these factors in turn influence sites and rates of deposition and resuspension of sediments and associated contaminants, as

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well as rates of contaminant release from bottom sediments to the over-
lying water column. Vertical gradients of contaminant concentrations
and other physicochemical properties are also present within bottom
sediments, reflecting the contamination history of the reservoir.

102. Longitudinal gradients also greatly influence the dynamics
of chemical contaminants in reservoirs, especially through the regula-
tion of sediment dynamics. As inflows enter the reservoir and plunge,
velocities slow and sediments are deposited on the reservoir bottom,
with coarser fractions nearer the headwaters and ever finer fractions
inflows approach the dam (Gunkel et al. 1984). Because finer sediments
typically have higher organic matter contents along with smaller parti-
cle sizes, they tend to be most contaminated. These fractions normally
settle out in the deep pool near the dam where anoxia is possible due to
vertical stratification, creating longitudinal patterns in sediment
properties and contaminant concentrations. Thus, the interaction of
vertical with longitudinal gradients may lead to the deposition of the
most contaminated materials in the deep pool where release rates are
likely to be highest due to bottom anoxia.

103. Lateral gradients in contaminant concentrations in sediments
may also be present, resulting from the fact that the highly organic
sediments in near-shore littoral zones serve as an excellent sink for
contaminants. All of these gradient-related factors influence contami-
nant concentrations in reservoir sediments and waters, as well as the
availability of contaminants to aquatic organisms. Clearly, such fac-
tors must be taken into account in the definition of sampling strata.

Location of pollutant sources

104. In those cases where specific sources of toxic pollutants to
reservoirs can be clearly identified (e.g., a point source discharge of
industrial wastes, PCB inputs via only one of several reservoir tribu-
taries), then the specification of sampling strata and sites should take
into account the location of these contaminant sources. This can be
accomplished by defining sampling strata as a series of concentric zones
radiating outward (e.g., downstream) from the pollutant source, or by
establishing one or more sampling transects originating at the source,

with discrete sampling points located along the transect(s) in a random or systematic random fashion.

Factors Influencing Sampling Frequency

105. Water quality problems are highly localized phenomena, both in space and in time, and they occur in neither a random nor a systematic manner in either dimension. The problem of sampling design reduces to making best use of all available information on the problem under study so as to obtain maximum useful data on the real-world populations of interest at minimum cost. Thus, as discussed in the paragraphs above, the allocation of sampling effort among discrete sampling strata involves taking into account existing information on spatial variability in those processes controlling the distribution and dynamics of the contaminants of interest in the study reservoir. In this way, variability in contaminant distributions over space is either reduced or partitioned into meaningful components, thereby producing an efficient sampling plan that balances resulting data reliability and representativeness against available resources. In the same way, the allocation of sampling effort over time, i.e., the determination of sampling frequency, involves using all available information on temporal variability in those processes regulating contaminant dynamics in the reservoir under study in order to divide the total sampling period (e.g., 1 year) into discrete temporal strata among which sampling effort is allocated. It is exactly because simple and systematic random sampling designs in time do not make use of available information on temporal heterogeneities in contaminant distribution and dynamics that they are generally less effective than stratified random sampling designs for determining sampling frequency.

106. The same total sample load may be processed in all three types of random sample designs. But, because it does take into account information on temporal variabilities in key regulatory processes, stratified random sampling is to be preferred as a means of determining sampling frequency (Gaugush et al. 1984, Khalid et al. 1983, Mills

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et al. 1982, Thornton et al. 1982). Thus, brief consideration must be given to the types of information useful for splitting the sampling period into discrete sampling periods or temporal strata.

107. Among the most important information to utilize in defining discrete temporal strata for sampling purposes is data on hydrologic processes, especially as related to in-pool hydrodynamics. The identification of both low- and high-flow events is important, the former because it indicates the potential occurrence of a variety of general water quality problems (e.g., anoxia, metals release from sediments), the latter due to the influence on sediment and hence contaminant transport into and within the study reservoir. Periods of snowmelt may also be critical in relation to contaminant and sediment loadings to and transport within impoundments. Data on temperature, precipitation, and other meteorological variables are also useful for defining temporal strata, in part since they influence reservoir thermal structure and also due to their effects on biological populations within reservoirs.

108. The timing of stratification cycles provides another source of important information relative to the identification of sampling strata in time. Sampling should be conducted during nonstratified (i.e., isothermal) periods, during times of maximum stratification, and when stratification is forming (spring) and breaking down (fall). Related to stratification cycles is the occurrence of periods of prolonged anoxia, in either hypolimnetic or metalimnetic regions of the reservoir, which should also be reflected in the definition of sampling frequency. Finally, information on behavioral changes, feeding habits, life cycles, and periodicity of biological populations inhabiting reservoirs should be taken into account. Such information is important because it indicates when reservoir biota may be susceptible to contaminant uptake from reservoir sediments or water, and also because it provides information as to when biota are readily sampled.

109. Clearly, all of these types of information are not independent; for example, anoxia typically occurs in the hottest part of late summer when the reservoir is most strongly stratified and flows are lowest, whereas high flows typically occur in spring when temperatures

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are still relatively cool and the reservoir is unstratified or weakly
stratified. Nor is the information required to define sampling strata
in time independent of that needed to identify spatial sampling strata.
However, these types of information must be considered in order to
define temporal sampling strata that are meaningful in relation to the
behavior of contaminants in reservoirs. EM 1110-2-1201 presents similar
recommendations for general water quality monitoring programs for reser-
voirs, and provides an example of stratification of the year into dis-
crete sampling periods based on the types of information discussed
above.

110. As discussed In Part III, preparation of a detailed sampling plan involves specification of what samples are to be collected, at what times, from what locations, and with what methods. Specification of a statistically sound and detailed sampling plan is essential to the success of a monitoring program. Yet preparation of such a plan is not sufficient to guarantee the success of the program or the soundness or utility of the resulting data. The plan must be implemented by well-trained personnel using standard sampling methods and apparatus, proper techniques for sample handling and processing, and appropriate quality assurance/quality control procedures. Program personnel must be thoroughly familiar with all procedures specified in the sampling protocol. Errors in executing the sampling plan will compromise the value of the resulting data, if not the entire monitoring program, and will render the subsequent analyses of samples for contaminant concentrations meaningless.

111. Thus, proper methods of sample collection, handling, preservation, and storage are essential to obtaining valid and representative results. Once samples have been collected and processed in accordance with the sampling plan, one must be able to assume that the samples are representative of both the original environments and the parent population(s) of interest, and that the samples do not change from time of collection through time of analysis. Otherwise, use of the standardized analytical methods specified in Part V and the proper quality assurance/ quality control procedures is of academic interest only. Because so many unique problems exist in relation to the sampling and analysis of toxic contaminants (e.g., Table 1), it is especially critical that sampling and sample handling be performed carefully to avoid compromising the integrity of the samples.

112. In order to avoid as many problems as possible in field sampling programs for reservoir contaminants, the following paragraphs present recommendations on the proper methods for sample collection and handling as well as sample containers, storage, and preservation.

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Table 6 summarizes recommendations on sample volumes, containers, preservation, and storage times. (Although this table summarizes currently accepted information on proper methods of sample handling for the indicated types of analyses, the reader should carefully consult the appropriate analytical methods detailed in Part V for any additional or specialized procedures required in processing samples for specific contaminant analyses, particularly for organic contaminants.)

113. Proper quality assurance procedures during field sample collection and handling are also discussed below. Much of the information summarized in this part is discussed in greater detail in many widely used sampling manuals; references to these manuals are provided in the following paragraphs. The following general manuals provided most of the information on sample collection, containers, storage, and preservation: ACS (1980); ASTM (1982); Brown, Skougstad, and Fishman (1970); Plumb (1981); US EPA (1979b, 1982); and USGS (1977).

Sample Collection and Handling

114. Proper sampling begins with the selection and correct implementation of documented and acceptable procedures and apparatus. The procedures and apparatus selected depend on the type of environmental sample being collected—water, sediment, or biota. General recommendations for each environmental sample type will be summarized separately.

115. Water samples may be collected manually using various types of sample bottles (e.g., Kemmerer, Van Dorn), or automatically using various types of pumps. In general, manual water sampling is preferable for contaminant monitoring programs. Where pumps are employed, the user must be careful to ensure that they do not in any way contaminate the sample in relation to subsequent sample analyses. For example, for analyses of organic contaminants, the pump should not contain any Tygon tubing and should have no oil on valves or other movable parts. Both USGS (1977) and US EPA (1982) discuss the advantages and proper use of manual versus automatic water sampling devices.

116. Water samples may also be taken as grab or composite samples. Composite water samples are more typical of stream sampling programs than of reservoir sampling. Also, it is difficult to employ composite sampling if constituents to be analyzed are subject to change with storage, if information on concentration variability in time and/or space is desired, or if temporal trends in contaminant variables are of interest. Again, USGS (1977) and US EPA (1982) provide informative discussions of the relative advantages of grab versus composite sampling as well as proper methods of compositing. In general, grab sampling of reservoir waters should be employed in contaminant monitoring programs (see also ASTM 1982; Brown, Skougstad, and Fishman 1970; and US EPA 1980).

117. Sufficient water volumes should be collected for all analytical tests planned. Table 5 summarizes recommendations on water sample volumes by chemical contaminant class (Table 3). (These may vary somewhat depending on the actual contaminant concentration in the sample.) Larger samples may be taken and then partitioned into subsamples for subsequent analysis if the methods of sample preservation and storage are compatible. Approximately 8 ℓ of water would be required to analyze a single sample of all of the contaminants considered in Part V of this report.

118. Depending on the contaminant(s) to be analyzed, it may be necessary to fill sample bottles completely, without the presence of air bubbles (Table 5). For example, for purgeable organics, bottles should be filled slowly to overflowing, covered with a septum, and sealed with an airtight screw cap; no air bubbles should be present. Except as noted in Table 5, conventional water sampling practices such as those summarized in ASTM (1982, Method D3370) should be employed (see also Brown, Skougstad, and Fishman 1970; Plumb 1981; US EPA 1980, 1982; and USGS 1977).

119. Since one will typically be interested in contaminant concentrations in filtered rather than bulk water samples, samples should be filtered as soon as possible after collection, either in the field or immediately upon receipt in the laboratory. In general, a 0.45-µm

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filter should be employed (AHPA 1981a, US EPA 1979b). To avoid problems
with sorption and contamination, especially for organic contaminants,
either glass fiber or metal-membrane filters should be employed. Once
bulk water samples have been filtered, one has a sample of suspended
sediments for subsequent analysis in addition to the filtered water
sample. Especially if one is interested in analyses of suspended
sediments, grab water samples using manual procedures are preferable in
order to avoid problems with sample heterogeneity and differential sam-
pling of suspended sediment size fractions.

120. Bottom sediments may be sampled with various types of coring
devices (e.g., piston-driven, gravity), dredges, or grab samplers. Use
of dredges for bottom sediment sampling leads to the collection of
large, well-mixed samples useful for qualitative analyses. Grab sam-
pling generally provides large samples of surface materials, whereas
cores generally provide the least disturbed sediment samples. Whichever
sampling approach is taken, the method itself must not introduce bias
into results due to differential penetration of the sampling device into
the sediments in relation to the occurrence of vertical gradients in
sediment characteristics. Core samplers are generally preferable in
this regard, and must be used if one is interested in examining vertical
trends in contaminant concentrations and other sediment properties.
Once samples have been collected, they should be placed into an appro-
priate type of sample container as discussed below; containers should be
completely filled without the presence of air bubbles. Plumb (1981)
provides a particularly thorough discussion of the collection and pro-
cessing of sediment samples for contaminant analyses; this reference
should be consulted for further details. US EPA (1979b) and USGS (1977)
also provide thorough discussions of sediment sampling methods.

121. Sampling of reservoir biota involves a variety of appro-
priate methods and types of equipment. In all cases, however, grab
rather than composite samples should be taken for biological analyses.
For planktonic organisms (phytoplankton, zooplankton), various types of
net and bottle samplers may be employed. Periphyton samples are ob-
tained by scraping various natural (e.g., rocks) or artificial (e.g.,

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Plexiglas plates) substrates found or placed into the desired sampling environment. Macrophytes are collected with appropriate clipping and harvesting techniques. Benthic macroinvertebrates may be sampled from natural or artificial substrates or through the use of grabs, cores, dredges, nets, or screens. Fish samples may be collected using appropriate electrofishing, netting, seining, or chemical sampling methods.

122. Because sampling methods for biological organisms in aquatic environments are summarized in such great detail in many other manuals, detailed discussions of these methods will not be duplicated here. Among the manuals the reader should consult for further information on proper sampling methods for reservoir biota, the following are the most complete in regard to contaminant and general water quality sampling requirements: Slack et al. (1973), US EPA (1982), USGS (1977, Section 4), and Weber (1973). General limnological sampling procedures for reservoir biota, water, and sediment samples are contained in Lind (1974), Welch (1948), and Wetzel and Likens (1979).

123. Once reservoir water samples have been collected, they should be handled as described in the following paragraphs, for use with the appropriate analytical methods summarized in Part V. The information below on sample containers, storage times, and preservation methods is summarized in Table 5. These recommendations also generally apply to the digests (metals analyses) and extracts (organic analyses) prepared from sediment and biological tissue samples. However, some additional guidance is provided below on the handling of sediment and tissue samples prior to digestion or extraction.

124. For sediment samples, the types of sample containers specified below and in Table 5 for water samples may also be employed. However, it may be more convenient to contain the sample in various types of plastic liners that fit inside sediment coring devices, or to extrude the sample carefully and quickly in the field into some other type of plastic bag. Once in the appropriate container, the sample should be preserved until it is extracted or digested. Sample processing should begin quickly, immediately if possible, to prevent significant sample alteration or deterioration (see recommended holding times specified in

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Table 5). In no case should sediment samples be stored longer than 4-7 days prior to being extracted or digested as specified in the appropriate analytical method.

125. The method selected for sediment sample storage and preservation depends in part on the type of analyses envisioned. Preservation of sediment samples for bulk chemical analyses is generally easier and less demanding than for detailed sample fractionation analyses. Samples for bulk analysis may generally be stored frozen, wet and refrigerated, or air dried. However, freezing and air drying may result in the loss of some chemical contaminants of interest, and should be used only if it is known that the specific contaminant(s) to be analyzed are not adversely impacted. Samples for detailed fractionation, as well as for many bulk analyses, must be stored in a wet state only, in a refrigerator at 2° to 4° C, in an airtight container protected from light. This should be regarded as the preferred method of sediment sample storage and preservation prior to extraction and digestion.

126. Once sediment samples are removed from storage, subsequent subsampling and processing should be performed under a nitrogen atmosphere within a glove box. It is also generally advisable to pass the sample through a No. 10 mesh (2-mm) screen in order to remove larger particles prior to further processing. Plumb (1981) provides detailed discussions of the processing of sediment samples for contaminant analyses (water samples also), including proper methods of storage, preservation, extraction, and digestion. Other useful discussions may be found in Baker (1980), US EPA (1982), and USGS (1977).

127. Biological tissue samples are stored, preserved, and processed in various ways depending on the specific types of samples involved. Planktonic organisms are typically stored in the same types of containers as specified for water samples. Periphyton may be scraped from various substrates into similar containers filled with water from the same environment. Both types of biological samples are often preserved with mercuric chloride (1 ml/ℓ) for up to 1 week. Samples of macrobiota (benthos, macrophytes, fish) are typically placed in plastic bags or wrapped in foil. Storage in a wet state, in a refrigerator at

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2-4° C in an airtight container protected from light, is probably the best method of sample preservation. Under some circumstances, samples may be stored frozen at -12° to -18° C or freeze dried. However, such procedures can result in the loss of some contaminants of interest. They should be employed only if it is known that they will not adversely impact the specific contaminants to be analyzed. As with sediment samples, biological tissue samples should be extracted or digested quickly, preferably immediately but certainly not later than 1 week after sample collection (see recommended holding times in Table 5).

128. Biological samples are frequently further fractionated or subsampled prior to digestion or extraction. For example, as dictated by study objectives and analytical methods, specific organs may be removed for analysis or soft tissues may be separated from hard body parts. Metals analyses require the digestion (wet or dry) of tissue samples, while organic analyses require some type of solvent extraction procedure. Grinding or maceration of tissues may be a required means of sample preparation prior to sample digestion or extraction. Various manuals, including the following, provide detailed instructions on the processing of biological tissue samples for contaminant analyses: APHA (1981a), Gaul and McMahon (1983), and US EPA (1980, 1982).

129. Once sediment and tissue samples have been digested and extracted properly, the resulting solutions can be treated further as specified for water samples. Thus, on the assumption that the sorts of procedures just summarized for collecting and handling samples of reservoir sediments and biota have been properly employed, no further distinction will be made in the following sections between water, sediment, and tissue samples.

130. Occasionally it may be necessary to ship or mail samples from the field site to the analytical laboratory for subsequent processing. In such cases, the times required for sample transit should be kept as short as possible to avoid sample degradation. Moreover, the guidance contained in footnote 5 to Table 5 should be followed in preparing samples for transit.

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Sample Containers

131. Selection of proper containers for contaminant monitoring programs should be based on consideration of the following container characteristics: size, weight, resistance to breakage, interference with chemical contaminants to be analyzed, cost, availability, and procedures required for container cleaning and preparation for sampling. Where the appropriate analytical methods call for the use of glass containers, containers made of either Pyrex or Kimax borosilicate glass are preferred. Such containers are inert and easy to clean. If analytical methods call for the use of plastic containers, those made of linear polyethylene should be chosen. In both cases, wide-mouth containers are best in that they are easy to fill and clean.

132. Table 5 summarizes recommendations on sample containers by chemical contaminant or contaminant class (Table 3). In general, for organic analyses, sample containers should be 1- to 2-ℓ borosilicate glass jars having Teflon- or foil-lined lids or septa, or Teflon- or foil-lined airtight, screw-on caps. For purgeable organics, 40-ml borosilicate glass vials with screw caps should be used. Septa for these vials should be made of Teflon-lined silica. For nonpurgeable organics, containers should be 1- to 2-ℓ amber glass bottles of French or Boston round design. Glass vials may also be used. Caps should be airtight, screw-on caps lined with Teflon or foil. However, the use of wide-mouth containers is not appropriate where sample interaction with the cap liner or outside environment is important.

133. Jars, lids, and liners used for organic analyses should be cleaned by washing for approximately 15 min in chromic acid, rinsed with tap water and then organic-free distilled water, and finally rinsed several times in redistilled, interference-free solvent (e.g., acetone, hexane, petroleum ether). Following air drying in a contamination-free environment, lids and liners should be placed on the jars, which should then be placed into a sealed container until used.

134. For metals analyses, containers should be 1-ℓ jars made of linear polyethylene having airtight, screw-on polypropylene caps without

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liners. Containers and caps should be washed in a nonphosphate deter-
gent, rinsed with tap water and then distilled-deionized water, soaked
in 1:1 analytical reagent grade nitric acid (up to 12 hr), rinsed with
3 to 5 portions of high-quality distilled water, and then drain-dried in
a clean environment. Jars should be capped and placed in a sealed con-
tainer until used. Note that, if necessary to remove organic stains,
containers may be initially washed in chromic acid rather than
detergent.

Sample Storage

135. Table 5 summarizes recommendations on maximum holding times
for samples to be analyzed for the indicated chemical contaminant or
contaminant class (Table 3). In general, these recommendations repre-
sent the maximum permissible times to store environmental samples prior
to extraction or analysis, assuming that samples have been stored in
proper containers and properly preserved. One should be especially
careful concerning prolonged storage of samples if chemical contaminants
to be analyzed are either chemically unstable (e.g., herbicides) or
volatile (e.g., phenols). Information contained in footnote 6 to
Table 5 should be carefully considered in determining storage times for
samples collected during reservoir contaminant monitoring programs.

Sample Preservation

136. Proper methods of sample preservation are essential to
guarantee sample integrity. Inasmuch as complete sample preservation is
impossible, one can only hope to retard the rate of sample change or
degradation. Preservation techniques are designed to retard biological
growth in the sample, hydrolysis, and adsorption, as well as to reduce
volatility. These techniques are generally limited to the following
approaches: chemical addition (to the sample container prior to field
sampling), pH control (to keep metals in solution), refrigeration (the
best all-around method), freezing (not generally recommended since it
may lead to loss of some contaminants), and protection from light (to
retard photolytic degradation of the sample). Alternative means of

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sample preservation may be employed if their effectiveness can be clearly established.

137. As summarized in Table 5, preservation of samples to be analyzed for organic contaminants involves various combinations of chemical additions, pH control, refrigeration, and protection from light. For metals analyses, refrigeration and pH control are the primary methods of sample preservation. Footnote 4 to Table 5 contains important information on the use of sample preservation techniques in reservoir contaminant monitoring programs.

Quality Assurance

138. Well-designed and properly implemented quality assurance procedures form an essential component of the overall monitoring program. Quality assurance refers to specific procedures followed during the conduct of the sampling program, as well as during subsequent sample processing and analysis, which are designed to ensure the accuracy, comparability, precision, reproducibility, reliability, and representativeness of sampling and analytical results of the monitoring program. Discussed in the subsections which follow are the coordination of quality assurance procedures; specific procedures involved in the preparation of field reagents, spiked and split samples, and reagent blanks; and procedures for documenting the chain of sample custody throughout the monitoring program. Most of this material was summarized from more extensive discussions in Lang et al. (1981) and US EPA (1979c). Other useful sources of information on quality assurance procedures include Bicking, Olin, and King (1978); Friedman and Erdmann (1980); Plumb (1981); Sherma (1976); Stratton and Bonds (1979); and US EPA (1982). Additional discussion of quality assurance policies and procedures is contained in Part VI of this report in relation to the conduct of monitoring programs under contract.

Coordination

139. Coordination in implementing the quality assurance program is achieved by establishing clear lines of authority and responsibility

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among project personnel, and by developing, documenting, and circulating
to all program participants a thorough and complete quality assurance
plan. This plan should cover all facets of the monitoring program, from
initial sample collection through sample analysis and data management,
analysis, and interpretation. The plan should also specify matters
related to personnel qualifications, training, and continuing education.
Specifically, the plan should delineate analytical criteria (precision,
accuracy, and limit of detection) for all contaminant variables of
interest; sampling program design as well as sampling and analytical
methods to be used; requirements for documentation of all field, labora-
tory, and chain-of-custody procedures; schedule of performance and qual-
ity assurance audits; schedule and procedures for equipment/instrumenta-
tion calibration and maintenance; requirements for data management,
review, and interpretation; and all other matters essential to proper
completion of the monitoring program.

140. Responsibility for proper and timely project completion
rests with the project manager, who also typically serves as the quality
assurance coordinator. His role in quality assurance matters is analo-
gous to that of the contract manager for contaminant monitoring studies
performed under contract. He is responsible for overall integration of
the quality assurance plan, for monitoring results of quality control
testing for all field and laboratory activities, and for screening re-
sulting data to detect errors prior to program completion. Direct
responsibility for day-to-day field and laboratory operations should
rest with the field crew chief and the laboratory supervisor, respec-
tively, who have been specifically appointed for this purpose.
Together, these three individuals are responsible for integrating all
aspects of the monitoring study. They are specifically responsible for
coordinating the proper placement in the field and subsequent laboratory
analysis of reagent blanks, spiked and split samples, and performance
test samples, as discussed in the subsections which follow.

141. The field crew chief and laboratory supervisor each is
directly responsible for: personnel training and supervision in his
respective environment; proper conduct of approved and acceptable

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sampling and analytical methods, as specified in the quality assurance plan; calibration, maintenance, testing, and proper operation of field and laboratory equipment and instrumentation; proper maintenance of chain-of-custody and other required records in appropriate logbooks; proper labeling of samples/sample extracts; and regular conduct of quality control checks and tests, as well as the reporting of quality control results to the project manager. Each should be knowledgeable concerning all aspects of the monitoring program under his respective supervision.

142. Part VI of this report contains field and laboratory quality control procedures appropriate for monitoring studies performed under contract. These procedures should also be implemented by the field crew chief and the laboratory supervisor for contaminant monitoring studies conducted in-house. Similarly, Parts VII and VIII contain what are essentially quality control recommendations which should be followed by the project manager in the data management and interpretation phases of the contaminant monitoring program.

Field reagents

143. Reagents and solvents used in field sampling should be of equivalent purity and quality to those used in laboratory analyses. Acids for field spiking and preservation of metals should be of analytical reagent (AR) grade or better. Low-temperature redistillation of such acids in borosilicate glass may be required to reduce background impurities to below detection limits. The minimum purity of reagents used in analyses of organic toxicants is again AR grade. Other, more stringent requirements for these reagents may exist depending on the analytical method used (i.e., even greater purity required in regard to certain classes of compounds, such as electronegative materials for electron capture detection in gas chromatography). For use with water and tissue samples, in which toxicant concentrations may be especially low, analytical requirements may dictate the use of pesticide-quality solvents. Reagent water prepared in the laboratory for field dilutions should conform to ASTM Specifications, Type I or II. Both Lang et al. (1981) and US EPA (1979c) provide more detailed recommendations

concerning the required purity of field reagents and solvents.

144. For field use, performance test samples should be prepared in the laboratory from EPA-certified check samples or other commercial sources, and provided to the field crew chief for random placement among field samples. Such samples are analyzed as a check on sample degradation and contamination resulting from field sampling and sample handling, preservation, and processing. These analyses are distinct from test samples which are prepared and analyzed in the laboratory, without transit to the field, in order to assess the accuracy of the analytical method employed for a given chemical contaminant and to develop and check instrument calibration curves (see paragraphs 202, 210, and 212).

Field sample spiking and splitting

145. Preparation in the field of reagent blanks, spiked samples, and split samples is prone to many sources of contamination. Nonetheless, along with the analysis of performance test samples as discussed in the previous paragraph, preparation and analysis of these sample types represents the only viable approach to determining sample degradation from time of sampling to analysis; sample contamination due to preservatives, distilled water, containers, or handling; sample homogeneity; and the accuracy, precision, and percent recovery of the analytical method(s) being used in a given contaminant monitoring study. Thus, careful preparation and analysis of all these sample types are essential ingredients of a proper quality assurance program. Laboratory analysis of test samples, reagent blanks, and spiked and split samples is discussed in Part VI as part of the Government quality assurance plan in managing contractor studies.

146. Spiked samples are prepared and analyzed in order to determine the degree to which sampling and sample handling, shipment, and storage have altered the sample in respect to its representativeness of the field environment from which it was collected. Such samples also provide a means of calculating the percent recovery of analytical methods employed in the monitoring study. Similarly, split samples provide information on sample homogeneity, help determine spike recovery, and provide a means of assessing the precision of laboratory analytical

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methods as well as the comparability of analytical results obtained from different laboratories or methods.

147. Spiking solutions should be purchased or prepared in the laboratory from primary standards dissolved in distilled water or water-miscible organic solvents for field use. Prepared spikes should be transferred in the field from the stock solution to a premeasured sample. Only duplicate (i.e., split) water samples should be spiked in the field; sediment samples should not be spiked at all. Spiked tissue samples should be prepared in the laboratory as discussed below. In preparing both the spiking solution and the spiked sample, proper quantitative transfer methods using clean volumetric pipettes must be followed. The identity of the spiked sample, the spike concentration, and the associated splits and reagent blanks must be recorded in the logbook.

148. Preparation of split samples involves thorough sample homogenization and splitting, as well as careful labeling of all splits and recording of the identity of split samples and associated spikes and blanks in the logbook. Splitting of water and sediment samples should be performed in the field, while the splitting of tissue samples should be done in the laboratory.

Reagent blanks

149. Reagent blanks are analyzed in order to provide a check on degradation or alteration of reagents in the field as influenced by such factors as time since preparation and exposure to contamination from sample containers and handling. Reagent blanks prepared in the field should be submitted for laboratory analysis along with all spiked and split sets of samples. Each blank should be prepared from high-quality distilled water plus the proper preservative for each type of sample and chemical contaminant being analyzed. In preparing reagent blanks, one should be aware of proper sample size for the appropriate laboratory analytical procedure to be employed. To be useful for their intended purpose, reagent blanks must be numbered, labeled and recorded, stored, and otherwise handled and processed as are all other field samples.

Tissue spiking and splitting

150. Spiking and splitting of tissue samples should be performed

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in the laboratory in a manner specified by the appropriate analytical
method (see Part V) employed for the particular chemical contaminant of
interest. In general, spiked and split tissue samples should be ana-
lyzed at the same overall frequency as water samples.

Chain of custody

151. Chain-of-custody procedures refer to steps taken in main-
taining an accurate written record of the receipt and disposition of
samples by all persons involved in sample collection and processing
during a contaminant monitoring program. Such procedures provide a
means of proving conclusively that samples have been in the custody of
authorized and trained personnel from the time of collection through
sample analysis and data interpretation. Proper understanding and
implementation of chain-of-custody procedures are essential to main-
taining the integrity of samples and for protecting study results from
legal challenge.

152. Lang et al. (1981) and US EPA (1979c) define sample custody
or possession and provide thorough examples of chain-of-custody proce-
dures appropriate to water quality monitoring programs; these sources
should be consulted for further details. In general, proper implemen-
tation of these procedures involves maintaining a custodial record in
bound notebooks, specifying the location and duration of sample storage
as well as sample handling for each step in sample processing, from
initial collection through analysis and disposal. Such records are
maintained by a sample custodian (e.g., field crew chief, laboratory
supervisor) appointed at each step of sample handling and processing.
The fewer the number of people handling a given set of samples, the
smaller is the danger of sample tampering or contamination. Samples
should be retained by the final custodian until permanently archived or
until it is permissible to dispose of them.

153. Once field samples have been collected and processed as specified in Part IV, they must be analyzed for the chemical contaminants of interest. The rigorous chemical analysis of environmental samples for toxic contaminants typically present in trace quantities presents a severe challenge to analytical chemists, and poses problems very different from those encountered in the analysis of more conventional pollutants. Because of this, only widely accepted and recommended methods specified in the most current editions of appropriate methods manuals should be employed in analyzing reservoir samples for concentrations of chemical contaminants. These methods must be thoroughly documented, validated, and tested, and carefully followed by a reliable and well-trained analyst. Any revisions of published methods must also be verified and documented.

154. The analytical methods to be used must be specified in the sampling or quality assurance plan for the overall monitoring program. The accuracy, precision, and limits of detection of the chosen analytical methods should also be documented in the plan. Proper quality assurance/quality control procedures as specified in Parts IV and VI of this report should be followed throughout the laboratory analysis portion of the project. Only if all these recommendations are followed will the monitoring program result in reliable and representative data which are scientifically acceptable and not subject to legal challenge.

155. The choice of analytical methods to be employed in a reservoir contaminant monitoring program should be based on the following criteria: (a) the methods selected should measure the constituent of interest with the desired levels of accuracy, precision, and specificity in the desired types of environmental samples; (b) the methods should employ the types of skills and equipment/instrumentation available in a modern analytical laboratory; (c) chosen methods should be in wide use, or at least be sufficiently used so that the validity of the methods is beyond question; and (d) methods should be sufficiently rapid for routine use with large sample loads. ACS (1980) provides an especially

succinct yet thorough discussion of the many factors to be considered in relation to the laboratory analysis of environmental samples for contaminant concentrations. Other valuable sources of information include APHA (1981a); Brown, Skougstad, and Fishman (1970); Gaul and McMahon (1983); Goerlitz and Brown (1972); Longbottom and Lichtenberg (1982); Plumb (1981); Sherma (1976); US EPA (1978, 1979b, 1979c, 1980, 1982); and USGS (1977).

156. It is the intent of this chapter to summarize the most widely used, recommended, and acceptable analytical methods for the toxic pollutants listed in Tables 2 and 3. A detailed listing of these methods is provided as Table 6. Thorough documentation of these methods would require many volumes and is clearly beyond the scope of this report. Such documentation is provided in the numerous manuals and reports cited in the footnotes to the table; these references should, of course, be consulted by the reader of this report for further details on the analytical methods cited. Although the methods cited in Table 6 are specifically designed for water samples, they may also be used for sediment and tissue samples that have been processed, digested, and extracted as described in Part IV and in the references cited therein.

157. In preparing Table 6, those widely used and readily accessible manuals which are directly relevant to contaminant and general water quality monitoring programs were consulted. The numerous footnotes following Table 6 provide additional details regarding the methods cited. This table is similar in organization and content to versions previously published (e.g., Federal Register, 1984, Vol 49, pp 43234-43442); however, unlike the earlier versions, Table 6 contains citations to methods in the most recent manuals of the EPA, USGS, ASTM, APHA, and AOAC (Association of Official Analytical Chemists).

158. Methods are cited in Table 6 for all contaminants listed in Tables 2 and 3 except asbestos and kepone. Analytical methods for asbestos have recently been published in an EPA study (Chatfield et al. 1983). Methods for kepone are contained in Gambrell et al. (1984). The Environmental Monitoring and Support Laboratory, US Environmental

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Protection Agency, Cincinnati, Ohio, can be contacted for detailed recommendations on analytical methods for kepone, as well as technical information on the proper implementation of the methods cited in Table 6. Technical questions can also be directed to the Analytical Laboratory Group, Environmental Laboratory, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

159. Although the methods cited in Table 6 are the most commonly recommended ones, current statutes (Federal Register, 1984, Vol 49) provide that alternative analytical methods may be employed, provided that these methods are thoroughly documented, tested, and verified, and known to produce reliable and representative results. The burden of proof concerning the acceptability of such alternative methods clearly rests with the laboratory or organization that wishes to employ them on a routine basis.

PART VI: CONTRACTOR SELECTION

160. It was suggested earlier in this report (paragraph 23) that deficiencies in existing contaminant monitoring programs in CE reservoirs are in large measure related to the newness of the concern with toxic chemicals, and to the fact that toxic pollutants pose new problems for water resource managers not encountered with more conventional pollutants (e.g., Table 1). One consequence of these new problems is that field and laboratory methods required to collect, process, and analyze reservoir samples for contaminant concentrations in the microgram/litre (water samples) or microgram/kilogram (sediment or tissue samples) range (or even lower) are more sophisticated and difficult to perform and require greater attention to quality assurance procedures than for the more conventional pollutants (ACS 1980, Ballinger 1979). Moreover, these methods require the use of new and highly sophisticated analytical instrumentation. Thus, greater training requirements exist for personnel conducting contaminant monitoring programs than for traditional water quality monitoring programs (Khalid et al. 1983).

161. In comparison with these needs, many CE Division and District offices may not have in-house analytical capabilities or personnel with adequate training to conduct monitoring programs for contaminants. This situation is further complicated by severe personnel limitations within many CE Division and District offices. Much of the work involved in a contaminant monitoring program, perhaps including both field sampling and laboratory analysis, may therefore have to be done under contract. However, conducting reservoir monitoring programs under contract raises concerns about the quality control procedures employed by the contracting organization, and ultimately about the reliability of the resulting data (Ballinger 1979, Khalid et al. 1983).

162. In order to avoid problems with the quality and reliability of data resulting from monitoring done under contract, guidance is provided here on the awarding and management of contracts to conduct contaminant monitoring programs, as well as on quality assurance procedures. The material that follows was summarized primarily from Engler

(1981) and Lang et al. (1981). Other useful sources of information include EM 1110-2-1201; Bicking, Olin, and King (1978); US EPA (1979c, 1982); Friedman and Erdmann (1980); Plumb (1981); Sherma (1976); and Stratton and Bonds (1979). These sources should be consulted for further details.

Types of Contractor

163. Available contractors may generally be classified into three broad categories: private firms, academic institutions, and other government agencies (Federal, regional, State). Although considerable variation exists among the contractors of each category, each contractor type offers certain advantages and disadvantages relative to the conduct of reservoir contaminant monitoring programs.

164. Private consulting firms are operated for profit, tend to be highly competitive financially, and have higher costs in conducting a given project than the other two contractor types. However, they are accustomed to working in a contracting environment, involving specific objectives and firm deadlines dictated by the funding agency. Moreover, they will often conduct a broad range of studies, from basic research to routine surveys. Such firms often exhibit great flexibility in conducting projects, as they can draw the required expertise from a diverse scientific and technical staff. Responsibility for project completion is typically clearly defined in such firms, with a project manager and specific staff assigned to a given project.

165. Costs for projects contracted to academic institutions may be quite low in comparison with the other two contractor types, in part due to lower overhead rates and to the use of student labor. The expertise available at such institutions, including both faculty and advanced graduate students, is typically great, so that highly competent individuals are available for conducting specific studies. If the institution is located near the reservoir in question, direct experience in working on that system as well as existing, site-specific data may be available. However, in at least some academic institutions, the focus is strictly

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on basic research; the faculty may be unwilling to become involved in routine monitoring studies. Also, many faculty are unaccustomed to working in a tightly controlled contracting environment, and may have their academic year schedules constrained by teaching responsibilities; their flexibility during times when classes are not in session is typically much greater. One other factor must be considered: responsibility for contract completion is not as clearly defined as in private firms. The contract is actually written with the institution; the faculty member who will conduct the work is the designated principal investigator, but there is no other project manager per se who will oversee project completion.

166. Monitoring programs can also be contracted to a wide variety of government agencies under interagency agreement. The availability and characteristics of agencies willing to participate in such agreements vary widely. In general, agency costs are intermediate between those of private firms and academic institutions. Those agencies which routinely participate in interagency agreements for water quality studies generally are willing to conduct a variety of studies, from routine to more basic; are familiar with working in a contracting environment; have internal management procedures that specify clear responsibility for proper and timely project completion; and have in-house expertise for conducting the work in a professionally competent manner. However, the availability and flexibility of such agencies to participate in interagency agreements may be constrained by their own internal priorities and missions. Also, the possibility exists that the agency's priorities can be redefined after the agreement has been initiated, thus affecting the manpower and expertise allocated to the monitoring program.

Contracting Methods

167. Several different methods exist for contracting reservoir contaminant monitoring programs. The preferred method involves the competitive selection of an appropriate contractor deemed to be technically

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qualified and capable of conduc　　　　desired program in a timely and
cost-effective manner. Competi.　　　.tractor selection may be accom-
plished through one of two processes:　formal advertising or
negotiation.

168.　Formal advertising involves an Invitation for Bids (IFB)
from all qualified contractors in a manner deemed necessary to ensure
full and free competition for services. Although formal advertising is
the preferred approach to competitive contractor selection, it has sev-
eral potential problems for use in contracting contaminant monitoring
programs. First, it is virtually impossible to specify in the IFB every
technical detail of the monitoring program to which the chosen contrac-
tor must adhere. Second, because this method does not involve the eval-
uation of contractor proposals, it is difficult to determine whether all
potential contractors who respond to the IFB are technically qualified
to carry out the program as desired.

169.　Competitive contractor selection via negotiation involves
evaluation of proposals received in response to a Request for Proposals
from all organizations deemed capable of performing the desired monitor-
ing. This approach has several advantages for use in monitoring pro-
grams. First, contractors can propose the use of techniques not
presently being employed by or familiar to the contracting Division or
District Office. This may result in cost savings or in technical im-
provements in the resulting study. Second, the ability to review pro-
posals from potential contractors will enhance identification of that
organization most technically capable of conducting the specified
program.

170.　In the somewhat unusual situation that only a single con-
tractor is available to carry out the desired monitoring program in a
technically competent manner, and the total program cost does not exceed
some specified value (typically $10,000-25,000), the contract can be
awarded under a sole source purchase order. Under the proper set of
circumstances, this is an acceptable and even desirable method of
awarding a monitoring contract.

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171. One may still be able to award the contract under purchase order if the maximum cost does not exceed the ceiling specified in the previous paragraph. In this case, competition is ensured by soliciting several different sources deemed capable of conducting the monitoring program. Generally, three to five sources are considered adequate.

172. Awarding the monitoring program to another government agency involves initiation of an interagency agreement with that agency. Under some circumstances, it may be possible to award monitoring contracts to firms listed on the Federal Supply Schedules (FSS) published by the General Services Administration. Because this method of contractor selection can often result in significant cost savings, the FSS should be reviewed periodically to determine whether contaminant monitoring programs can be accomplished via this method of contractor selection.

Contracting Process

173. The contracting process involves a series of sequential and well-defined steps, beginning with the decision to conduct a specific monitoring program under contract and terminating with the contract award. However, these steps do not necessarily need to be followed in rigid fashion. Within reasonable bounds, the overall process can be used creatively in order to realize the desired monitoring goals. Throughout the contracting process, the project manager should work closely with procurement personnel, and should allow sufficient time so that the procurement can be accomplished properly and with required flexibility. Frequently, the process takes up to 6 months before the final contract is signed by both parties involved. The discussions which follow focus primarily on competitive contractor selection via formal advertising and negotiation. Procurement via other contracting methods discussed in the previous section involves modification of the procedures followed in these two basic methods of contractor selection.

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**Competitive procure-
ment via formal advertising**

174. By definition, formal advertising is a method of selecting a
contractor as a result of competitive bidding procedures. The method
requires the solicitation and evaluation of bids from potential contrac-
tors and award of the contract to the lowest responsive and responsible
bidder. Procurement via formal advertising involves the following
steps: determination of need for contracting; preparation and internal
review of detailed scope of work (SOW); preparation of IFB; preparation
of Government cost estimate (this step may be omitted); distribution of
IFB widely so as to maximize competition; formal opening and evaluation
of bids; selection of contractor; awarding and execution of contract.
It is the preferred method of competitive procurement unless negotiation
is specifically authorized by law. However, as discussed earlier (para-
graph 168), this method has several drawbacks for use in selecting con-
tractors for monitoring programs.

175. If formal advertising is to be a workable procedure for
selecting a contractor and realizing stated monitoring goals at a rea-
sonable cost, several requirements must be met. First, the IFB must be
prepared in sufficient detail that potential contractors know exactly
what they are bidding on and can respond appropriately. Second, a com-
petitive market for contractor services must exist, i.e., at least two
potential contractors must submit bids in response to the IFB. Third,
given at least two responsive bids from responsible contractors, the
award must go to the lowest bid. Finally, sufficient lead time must
have been allowed that all procurement steps can be followed properly.
If any of these requirements is not met, the procurement process will
suffer and it may be necessary (and authorized) to contract via
negotiation. For monitoring studies, the key shortcomings may be
(a) the inability to specify sufficient details of the desired monitor-
ing program in the IFB, and (b) the submission of at least two respon-
sive bids from potential contractors that can be judged to be techni-
cally responsible based solely on their bids.

176. Essential to successful procurement via formal advertising is a thorough and clearly written SOW. The required level of detail depends on the exact nature of the monitoring program; in general, sufficient detail should be included that no ambiguity in project purposes or design exists. A detailed scope is even more critical to procurement by formal advertising than by negotiation. In a sense, the SOW for this method of competitive procurement should be written with as much detail as though the study were being performed in-house by Government scientists.

177. The SOW should contain a clear and concise statement of monitoring objectives; thorough discussion of the relationship of the monitoring program to other ongoing projects; clear discussion of sampling and analytical methods to be employed; a concise statement of analytical methods and detection limits; thorough specification of program milestones and report submission requirements; specification of approaches to be followed in analyzing monitoring data and interpreting study results (if this is not to be done in-house); delineation of contractor quality control and quality assurance requirements; and any other detailed specifications or requirements deemed necessary to ensure that the monitoring program is carried out reliably and as desired.

178. The level of detail should be neither so narrow as to needlessly restrict contractor flexibility, nor so broad that items peripheral to the main purposes of the monitoring program can be explored. A thorough, well-written scope will (a) eliminate many potential problems that could arise during the conduct of the monitoring program; (b) clearly define the contractor's obligation and thereby protect the Government's interests; (c) provide the contractor with sufficient information to prepare a responsive bid and to conduct the study as desired; and (d) enable the contract manager and contracting officer to determine whether the contractor has complied with the terms of the contract.

179. For competitive procurement via formal advertising, a procedural requirement exists that the scope should be as free of technical language as possible. Instead, the scope should be written clearly in conventional language understandable to persons of diverse backgrounds

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(e.g., attorneys, accountants, procurement personnel); the technical content of the SOW should be reduced to essential information. This requirement again constrains the applicability of procurement via formal advertising to the contracting of technical monitoring studies, and makes procurement via negotiation a more desirable approach. The scope which meets the procedural readability requirement may be technically lacking, whereas the scope which contains sufficient technical detail to ensure the success of the monitoring effort may not satisfy the procedural criterion of readability to persons of diverse backgrounds.

180. Although not mandatory, preparation of a Government cost estimate may help to ensure that the contract award is both fair and reasonable. If prepared, this estimate should include all facets of the study which will be included in the contractors' cost estimates. These same comments apply to contracting via negotiation.

181. The IFB is a formalized document requesting potential contractors to offer to contract with the Government under the terms and conditions stated therein. Once prepared, it must be distributed widely to ensure significant competition. Bids received in response to this invitation must be formally opened and evaluated as to their responsiveness and the responsibility of the bidder. A bid will be judged unresponsive if it does not conform to the essential requirements of the invitation. Substantial deviations from terms stated in the IFB cannot be waived once bids are opened. Bids, including the apparent low bid, may also be rejected if it is determined that the bidder is not technically or generally responsible. Bid evaluation may involve many factors, including preaward visits to inspect the lowest bidder's facilities. Following bid evaluation, which includes consideration of price and other factors, the award is made to the lowest responsible bidder.

Competitive procure-
ment via negotiation

182. Procurement by negotiation should be followed under conditions authorized by law and whenever it furthers the public interest. However, the decision to follow procurement via this method does not eliminate the requirement to obtain maximum competition consistent with

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contracting needs. The Defense Acquisition Regulation (DAR) identifies seventeen conditions or exceptions under which negotiating authority is provided. The most important of these in relation to the conduct of contaminant monitoring programs are contracting for: (a) personal or professional services; (b) services of educational institutions; (c) supplies or services for which it is not practicable to contract via formal advertising; and (d) experimental, developmental, or research work.

183. Each negotiated contract must contain reference to the specific authority under which it was negotiated. Note that the DAR also contains procedural and contracting formalities that must be observed when procuring by negotiation. Division or District counsel and procurement personnel should be consulted concerning authority to contract via negotiation and the procedures required.

184. Under contracting by negotiation, the formal procedures and somewhat rigid rules of contracting via advertising need not be followed. Instead, proposals (RFP) or quotations (RFQ) are requested from all qualified contractors. On the basis of the proposals or quotes received, a contract is negotiated with that contractor making the best overall offer to the Government. During the negotiation phase, price bargaining may or may not be involved, depending on whether or not the most favorable offer received is fairly and reasonably priced. Again, a number of steps are involved: determination of need for contracting; preparation and internal review of detailed SOW; preparation and distribution of RFP (RFQ); preparation (optional) of Government cost estimate; evaluation of proposals (quotes) received; negotiation with contractor(s) in competitive range; (possible) evaluation of negotiated proposals (quotes); selection of contractor; and awarding and execution of the contract.

185. As with procurement via formal advertising, preparation of a detailed and carefully written SOW is essential to contracting by negotiation. Guidance on information to be included in the scope (paragraph 178) applies here as well. However, the scope prepared for this method of competitive contractor selection need not be as detailed as

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for procurement via advertising. Preparation of a less stringent SOW allows potential contractors greater latitude in preparing their proposals (quotes), encourages innovation and cost effectiveness in program design, and therefore provides an excellent basis for evaluating competing proposals (quotes).

186. The RFP (or RFQ) distributed to potential contractors should provide sufficient information to allow preparation of complete proposals (quotes) that are responsive to monitoring program requirements. Among the items to be included in the request are a clear and concise statement of monitoring objectives; the SOW; instructions on naming of the principal investigator and other key personnel, including specification of responsibilities and levels of participation for each investigator; detailed instructions on technical and pricing matters; description of the anticipated level of Government participation (if any) in the monitoring program; appropriate forms for cost estimates; any requirements for a listing of recent and/or current Government contracts; thorough specification of proposal (quote) evaluation criteria; address and deadline for proposal (quote) submission; address for further information, along with any stated restrictions on obtaining additional information; and any other information deemed necessary for the submission of complete and responsive proposals (quotes).

187. In order to ensure maximum competition, the RFP (RFQ) must be issued to as large a group of potential contractors as possible. Once proposals (quotes) have been received, they must be evaluated by a panel of reviewers of diverse backgrounds. Both numerical and narrative reviews of each proposal or quote should be prepared. The overall goal of the review process is to identify either the top contractor or the contractors in the competitive range for negotiation, as well as the items to be negotiated. The criteria for evaluation should have been established early in the contracting process, and should be known to potential contractors prior to proposal or quote submission (e.g., published in the RFP/RFQ as previously suggested).

188. The review process should focus on the technical soundness of the work proposed, the degree of innovation exhibited, the degree of

compliance with the RFP/RFQ, qualifications and experience of the participating investigators, cost, available facilities, and work schedule. In general, technical competence should take precedence over business matters. However, considerations of cost may be quite important, especially if the review reveals several contractors of nearly equal competence. Also, a contractor's cost (and time) estimates may reflect his understanding of the technical matters involved.

189. If a thorough and detailed SOW has been included with the RFP (RFQ), contractor qualifications and experience will be weighted more heavily than technical matters, which would be of more significance if contractors are allowed to design the details of the study. Reviews should pay particularly close attention to whether especially well-qualified and (possibly) well-known investigators will actually participate directly in the study or only serve as technical "consultants" (i.e., window dressing).

190. Negotiation begins once the top contractor or contractors within the competitive range have been identified by the review process. Negotiation involves considerable judgment on the part of all parties involved in order to reach mutual agreement on a final contract acceptable to both the chosen contractor and the Government. This may involve reviewing negotiated proposals (quotes) submitted by each contractor in the competitive range prior to a new deadline. Both technical and cost considerations may be included in the negotiations. Once the negotiated proposals (quotes) have been reviewed by the same panel that participated in the initial review, a final contractor is chosen, and the contract is awarded and executed. Again, this may involve such factors as preaward site visits or the submission of test sample analyses.

Procurement via
other contracting methods

191. Other contracting methods involve modifications of the steps just summarized. For most of these methods, the steps involved are simpler and less time consuming. In the case of sole source purchase orders and interagency agreements, no advertising or solicitation is involved. However, it is perhaps even more critical that a clear and

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detailed SOW be prepared and that the final contract be carefully nego-
tiated so as to be acceptable to both parties involved. For contracts
initiated under non-sole source purchase orders, the procedures involved
are essentially identical to those described for procurement via nego-
tiation, except that a shorter time period is involved and fewer
responses typically need to be reviewed.

Monitoring Contractor Performance

192. Once the contractor has been selected and the contract
awarded, attention must turn to managing the contract and monitoring
contractor performance. This is clearly the most critical and time-
consuming portion of the entire contracting effort. The contracting
organization cannot tacitly assume that the chosen contractor will per-
form the monitoring study in a timely and proper manner. Unless con-
tract management is done in an active and careful manner, on a regular
basis, the quality, reliability, and applicability of the results of a
given monitoring study cannot be guaranteed. Methods of contract man-
agement will vary widely depending on the duration, complexity, and
nature of the monitoring study being completed under contract, as well
as on the type, expertise, and reputation of the contractor performing
the work. However, some general guidance on useful approaches to moni-
toring contractor performance can be provided.

193. A contract manager should be appointed to monitor each con-
tract awarded. This individual should be capable of interacting
directly with the contractor on technical matters, should possess sig-
nificant expertise directly related to some substantial portion of the
overall monitoring study, and should have been involved throughout the
contracting process described in the previous section. Depending on the
size and complexity of the study being conducted, secondary managers
having expertise relevant to specific aspects of the study may also be
involved. However, the appointed contract manager should have primary
authority for ensuring overall contract completion.

194. The purposes of monitoring contractor performance are numerous, including the determination of whether (a) adequate progress is being made in comparison with the proposed time schedule; (b) the scope is being met, with no significant deviations; and (c) proper attention is being given to quality assurance/quality control procedures in all aspects of the monitoring study. In addition, monitoring allows the contract manager to correct or address unanticipated conditions. Periodic performance monitoring throughout the life of the contract will help in determining the need for future funding for continuation of the contracted study or initiation of related or followup studies. Periodic (e.g., quarterly or semiannual) visits, meetings, and/or workshops, involving both the contract manager(s) and contractor representative(s), should be held in order to review in detail the accomplishments since initiation of the monitoring study. During the time between meetings, frequent contacts (e.g., by phone) between the contract manager and contractor will reveal whether the study is progressing satisfactorily.

195. Essential to the management of monitoring contracts is the submission and careful review of contractor reports. The schedule for report submission should be specified in the contract and strictly adhered to by the contractor. Interim progress reports should be required at regular intervals, dependent on the duration and nature of the monitoring study. Such reports should focus on overall study progress, data acquisition and verification, and quality assurance/quality control considerations. Reports should be reviewed thoroughly by the contract manager and other secondary managers as appropriate, with prompt feedback provided to the contractor on problems discovered. Near the end of the study, a draft final report should be submitted and subjected to careful technical review by several individuals with expertise relevant to the monitoring study, including the contract manager. Review comments should be incorporated into the final report prior to the termination of the contract period.

196. One final aspect of contract management relates to quality assurance considerations. Careful attention to quality assurance procedures is critical to the reliability of monitoring data on contaminant

concentrations in reservoir waters, sediments, and biota. Thus, a quality assurance plan must be developed early in the contracting process. This plan must guide preparation of the scope of work, and should be instrumental in selecting a contractor to conduct the monitoring study. For use as a postaward contract management tool, the quality assurance plan should specify data verification procedures and minimum acceptable performance and quality contr⁻¹ activities which must be conducted and documented by the contractor. The plan should also specify the quality assurance requirements of the prime contractor relative to work performed by any subcontractors who participate in the monitoring study. Because of the importance of quality assurance to the proper conduct of contaminant monitoring studies under contract, this subject will be considered further in the following section.

Quality Assurance Program

197. In a general sense, quality assurance refers to actions taken during the course of a study to ensure that field and laboratory quality control policies and procedures are being properly implemented. Quality control refers to field and laboratory actions taken on a regular, day-to-day basis to achieve a desired level of accuracy, comparability, precision, reproducibility, and reliability in the results of sampling and analytical procedures. With specific reference to the conduct of contaminant monitoring programs under contract, Government quality assurance refers to testing, evaluations, and inspections performed by the Government in verifying that (a) the contractor conducts the monitoring study in compliance with contract requirements; (b) final results meet stated contract criteria; and (c) the contractor's field and laboratory equipment and instrumentation, personnel, and sampling and analytical procedures are adequate for proper quality control procedures.

198. Similarly, contractor quality control refers to testing and inspections performed by or on behalf of the contractor in controlling his procedures, equipment, materials, and personnel so that contract

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requirements are met in a satisfactory manner. The exact manner in which quality assurance and control policies and procedures should be designed and implemented will depend on the details of a given monitoring study and on the extent of the contractor's involvement (i.e., only field sampling, only laboratory analysis, both field and laboratory participation). Nonetheless, general guidance on both Government quality assurance and contractor quality control can be provided. The success of the entire study may depend on how these general points are implemented specifically for that study.

Government quality assurance

199. The Government's quality assurance program is coordinated by the contract manager. He is responsible for ensuring that all aspects of the contracted study are conducted properly, that the contractor's quality control policies and procedures are appropriate, that they are being followed regularly, and that the results of quality control tests are acceptable. The goal of the overall quality assuranco program is to ensure that any problems in data resulting from the monitoring study are detected and corrected prior to the end of that study. The contract manager realizes this goal by maintaining direct contact with the contractor's quality control supervisor and project manager (they may be the same individual), and by reviewing carefully contractor progress reports as they are submitted to detect problems in study results or inadequacies in the contractor's routine quality control procedures.

200. At the initiation of the project, especially when working with a contractor for the first time, the contract manager should carry out the comprehensive quality assurance program as specified in Section 6.5 of US EPA Handbook (1979c). This requirement should be specifically stated in the contract. During the course of the monitoring study, quality assurance procedures should ensure that the contractor's internal quality control testing comprises 15--20 percent of his total analytical effort, and should involve the analysis of performance test samples, spiked and split samples, and reagent blanks. The contract manager is responsible for the conduct of these analyses and should submit the proper materials in such a manner that the contractor does

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not know the identity or the contaminant concentration in the samples to be analyzed. The contract manager should carefully monitor the results of these analyses and should develop quality control charts based on the test samples submitted to the contractor.

201. If problems develop which cannot be easily resolved, the contract manager should employ the services of a referee laboratory to ascertain the exact nature of the problems discovered (e.g., can they be traced to field or laboratory procedures?). Based on the outcome of these analyses, the contract manager may require the inspection of the laboratory or the evaluation of field sample collection and handling procedures.

202. For quality assurance purposes, commercially available or EPA check samples should be used for the analysis of performance test samples. However, if appropriate materials are not available, they can be prepared with proper care from distilled water samples spiked with high-quality standards for the chemical contaminant in question. In general, one performance test sample should be analyzed for approximately every 25 samples analyzed. Results must be carefully examined by the contract manager to determine whether the laboratory is performing with acceptable accuracy (for test samples not transported to the field) as well as whether significant sample degradation and/or contamination are occurring (for test samples placed in the field).

203. For many contaminants and sample types of interest, performance test samples may be unavailable or hard to obtain. In such cases, spiked water samples may be analyzed as a substitute. However, spiked sediment or tissue samples should not be used for this purpose. Also, as a general rule, roughly every 25th field sample should be spiked; both spiked and unspiked portions of the sample should be analyzed. Results of such analyses can be used to calculate the percent recovery of the analytical procedure employed, and also provide information on the degree to which sampling and sample treatment have altered the sample in terms of its representativeness of the environment from which it was collected.

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204. The third type of sample analyzed for quality assurance purposes, split samples, provides a means of assessing the contractor's analytical precision, as well as examining comparability of results among two or more contractors. A sample to be split should be thoroughly homogenized and divided into at least two subsamples; each subsample should be independently analyzed, by the same or several contractors. As before, approximately every 25th-30th sample should be split for quality assurance purposes. This recommendation applies to sediment and tissue samples as well as to water samples.

205. Reagent blanks, the final sample type analyzed for quality assurance purposes, provide information on degradation and contamination of reagents used in field sampling. Appropriate reagent blanks should be submitted for analysis along with each set of spiked and split samples.

206. If the contractor is conducting only the laboratory analysis portion of the monitoring contract, the contract manager is responsible for the proper submission of performance test samples, reagent blanks, and spiked and split samples for analysis. However, if the contractor is conducting both field and laboratory components of the study, he is responsible for the spiking and splitting of field samples and the preparation and field placement of reagent blanks. In this case, the Government's quality assurance testing essentially involves strictly the submission and analysis of performance test samples. Nonetheless, the contract manager should still ensure that the contractor is conducting reagent blank and spiked and split sample analyses properly and at the same rate as though the Government were conducting the study.

207. The Government quality assurance program should also include consideration of those quality assurance items discussed in the final section of Part IV of this report.

Contractor quality control

208. The contractor must develop a written internal quality control program and make it available for review and retention by the contract manager. This plan should focus on all procedures which comprise the monitoring study, including equipment and instrumentation,

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calibration and maintenance, reagents and supplies, data management and
analysis, sample collection and analysis, and personnel training and
continuing education. In a very real sense, discussions contained in
all other parts of this report represent factors which should be con-
sidered in such a quality control plan.

209. Quality control considerations for field sampling should be
thoroughly outlined in the written sampling program or plan. This pro-
gram should delineate all details of sample location, collection, and
subsequent treatment. Sampling equipment should be routinely tested,
calibrated, and subjected to manufacturer's recommended maintenance pro-
cedures. Similarly, sampling methods should be regularly evaluated to
determine whether they are indeed sampling the target population. Ran-
dom quality control checks should be performed on all procedures for
sample location, collection, and handling to ensure that proper methods
are being followed as desired.

210. Minimum contractor quality control requirements for labora-
tory analyses are outlined in several of the references cited earlier
(paragraph 162). In general, these minimum requirements include speci-
fication of the following: (a) fraction (15-20 percent) of the total
analytical effort to be devoted to quality control testing; (b) inclu-
sion of sample replication, percent recovery determinations (preferably
from spiked sample analyses), and performance test sample analyses in
the quality control testing; (c) analyses of reagent blanks on each ana-
lytical run (not included in the above percentage); (d) establishment
and maintenance of instrument calibration curves; (e) use of standard
addition techniques for atomic absorbtion analyses; and (f) development
of quality control charts from test sample analyses.

211. Special quality control precautions must be taken for any
organic contaminant analyses via gas chromatography. Among those pre-
cautions which should be specified in the quality control plan are the
following: (a) injection procedures and precautions; (b) quality of
standard solutions; (c) procedures for maintaining the integrity of test
samples and reference materials; (d) proper methods for checking the
deterioration of stock and standard solutions; (e) requirements for the

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redistillation of solvents to remove interfering substances; (f) requirements for proper chromatograph operation at optimum conditions; (g) specification of the range of linearity for chromatograph operation; and (h) procedures for daily monitoring of chromatograph performance.

212. The quality control plan should also specify the schedule and procedures to be followed in calibrating and maintaining laboratory equipment and instrumentation. Equipment and instruments should be calibrated using NBS (National Bureau of Standards) standards whenever they are available, or other acceptable methods when they are not available. Similarly, equipment and instruments should be routinely maintained and serviced as specified by the manufacturer. Calibration and maintenance should be carefully documented, and such documentation should be available for inspection by the contract manager.

213. Also included in the quality control plan should be considerations relating to contractor data reports, i.e., specification of significant digits, units, and limits of detection and quantitation. The plan should further specify the manner in which both monitoring data and results of quality control testing will be included in regular progress reports to the contract manager, and should indicate plans for the retention (duration and method) of field samples/sample extracts and raw data.

PART VII: DATA MANAGEMENT

214. Once field samples have been collected and analyzed for concentrations of chemical contaminants of interest, the resulting data must be processed in a manner that facilitates subsequent data storage, analysis, and interpretation. This requires the establishment of general procedures for data management. For such procedures to be effective, one must assume that all previous steps in the monitoring program have been conducted in a technically and legally defensible manner, that is, data must have resulted from a properly designed and well-executed sampling program, and from acceptable and properly documented methods of sample handling and laboratory analysis, with careful attention throughout to proper methods of quality assurance.

215. The goal of data management is to facilitate (a) storage of reliable data in a form accessible by others, (b) subsequent analysis of data in relation to the stated study purposes, (c) interpretation of analytical results in relation to management needs, and (d) effective communication of results and management decisions to others. It is just as important to practice proper techniques of quality assurance during the data management phase as during earlier phases of a monitoring program. Otherwise, the reliability of the data cannot be guaranteed, and their usefulness for the purposes for which they were collected will be limited.

216. Because monitoring data must be managed for a wide variety of possible uses and users, blanket recommendations on the establishment of data management procedures for a contaminant monitoring program cannot be given. The general discussions contained in this part of the report will focus on the initial screening of laboratory data; available data base management systems as well as proper steps for data entry, editing, and retrieval in a given data base; and useful approaches for summarizing and analyzing data resulting from a reservoir contaminant monitoring program.

Initial Screening of Laboratory Data

217. As summarized in Part V, valid and legally acceptable analytical chemical methods must be used to generate data on concentrations of chemical contaminants in samples of water, sediments, and biota from CE reservoirs. This requires strict adherence to rigorous analytical procedures such as those outlined in ACS (1980). These procedures guarantee that raw measurements on field samples are converted into meaningful data that are interpretable in relation to study objectives. All resulting laboratory data must be carefully screened before they are entered into a data base management system or analyzed, to ensure that they do not contain errors that would compromise their utility.

218. Two analytical concepts central to the initial screening of laboratory analyses of environmental samples are the limit of detection (LOD) and the limit of quantitation (LOQ). The entry of limits of detection directly into the STORET water quality data base maintained by the EPA, as though they were actual sample measurements, was one of the most persistent problems in data base management identified by Khalid et al. (1983) in their survey of potential contaminant problems in CE reservoirs. Because proper understanding of these concepts is essential to the correct interpretation of data resulting from contaminant monitoring, the analytical basis for these concepts will be briefly summarized. ACS (1980) should be consulted for further details.

219. Both the LOD and the LOQ are related to random errors in laboratory measurements of chemical concentrations, assuming that all practical means of controlling systematic errors have been employed. That is, both are related to the estimate of the precision of the validated analytical method being used. Assume that the concentration of some specific chemical, termed the analyte by analytical chemists, is being determined. The concentration C of the analyte is related to the magnitude of the signal S measured on some specific piece of analytical equipment (e.g., peak height on a gas chromatogram, digital counts measured by atomic absorption spectrophotometry), through the response function $S = f(c)$. In graphical form, the response function is known as

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the calibration curve. The total signal measured for a specific environmental sample is composed of a part due to tne analyte and a part due to the blank or background contribution. Independent measurement of the blank signal allows calculation of the net analyte signal by difference.

220. The precision of the analytical method is related to the absolute variability in the response signal and is defined by the standard deviation of the net analyte signal. Since the net analyte signal is the linear difference between the total and blank signals, its standard deviation includes contributions due to variability in both.

221. The limit of detection is the smallest analyte concentration that can be reliably detected by the analytical method. It is defined by the extent to which the total signal exceeds the blank signal. ACS (1980) recommends a factor of 3 above the mean blank signal.

222. Similarly, the limit of quantification is the smallest analyte concentration that can be reliably quantified. Because reliable quantification is a more severe requirement than detection, the LOQ should be above the LOD. How much above depends on such factors as the precision of the analytical method being employed, the purposes of the study, and the applicable water quality criteria and standards. ACS (1980) recommends that the LOQ should be at least a factor of 10 above the mean blank signal.

223. These definitions of the LOD and LOQ influence the manner in which laboratory data on contaminant concentrations in samples of reservoir waters, sediments, and biota are to be reported and interpreted (ACS 1980). Concentrations below the detection limits are not detectable with any degree of certainty; such concentrations should be reported as not detectable, with the LOD given in parentheses. Concentrations between LOD and LOQ are detectable with a degree of certainty, though the exact numerical value is somewhat uncertain. As the concentration increases above the LOQ, the numerical reliability of the analyte concentration increases. Numerical values for concentrations within the region of detection should be reported, with the LOD again given in parentheses. The numerical significance of such values must always be considered in relation to the LOQ, however.

224. The recommendation of ACS (1980) concerning the value of LOD is probably quite adequate for the purposes of reservoir contaminant monitoring programs. A useful value of LOQ, however, is somewhat less certain. The value of the parameter may vary across monitoring programs and for different chemical contaminants in relation to the precision of the analytical method being used, the purposes for which the data were obtained, and the existing water quality criteria and standards.

225. Special attention should be given to situations in which the specified LOD or LOQ is greater than the existing criteria. In such a circumstance, the analytical method employed is so imprecise that no meaningful conclusions concerning possible violations of water quality criteria can be reached.

226. All data resulting from laboratory analyses of environmental samples should be carefully screened to ensure that they conform to the rigorous definitions of LOD and LOQ summarized above. In particular, concentrations below the LOD must be reported as not detectable; numerical results should not be reported for such samples. Laboratory analytical data should also be carefully subjected to other sorts of screening procedures before they are entered into data base management systems. If automatic laboratory data acquisition systems are employed, then their accurate and reliable functioning should be periodically reviewed. All equations and algorithms used to convert raw measurements made with analytical equipment to data on contaminant concentrations should also be checked at regular intervals. This includes all laboratory calibration curves, which should be updated periodically for any changes in instrumental sensitivity and reliability. All data forms generated in laboratory analyses, whether manually or automatically, should be carefully filed for subsequent reference in the event that questions arise concerning the accuracy of specific analytical results.

227. All analytical methods used in a given monitoring program should be carefully documented. Such documentation should include specification of the values of LOD and LOQ for each individual chemical contaminant. Any other useful methods of initially screening laboratory data to ensure that only reliable and meaningful data are entered into

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data base management systems must also be employed. Entry of questionable or erroneous data into a water quality data base can compromise the purposes of a given monitoring program and must therefore be prevented.

Data Base Management

228. Because the volume of data generated in water quality monitoring programs is typically so large, the use of manual procedures for data storage and analysis is impractical. Thus, a key component of a reservoir contaminant monitoring program involves establishment of a comprehensive computer-based data base management system. By definition, a data base management system involves a combination of personnel, computer hardware, and computer algorithms for the storage, retrieval, analysis, and display of raw data as well as analytical results (Saul et al. 1982). The purpose of such systems is to provide a structured approach to processing large quantities of data into useful results on which sound management decisions can be based. To be useful, a data base management system should provide easy access to all potential users. Sufficient documentation should be available to enable users to take advantage of all features of the system. The system should facilitate maintenance of individual data files and periodic updating. The management system should also have available a wide array of capabilities for analyzing and displaying stored data (Saul et al. 1982).

229. Commercially available data base management systems can be classified into two broad categories, general purpose and special purpose. General purpose systems focus mainly on strategies for data base construction and algorithms for the storage and retrieval of information. The analysis of stored data typically is not a major concern of most general purpose systems. By contrast, special purpose systems tend to simplify data base management and data storage and retrieval strategies. These systems focus on providing a wide array of statistical and mathematical routines for analyzing stored data. Table 7 summarizes relevant information on six commo `` used general purpose data base systems, while Table 8 provides similar information on five routinely

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used special purpose systems. Other systems are also available, but the eleven systems summarized in Tables 7 and 8 are those most frequently used in water quality monitoring programs, especially by CE Division and District Offices.

230. Which system is chosen for use in a specific reservoir contaminant monitoring program will depend on the requirements of that specific monitoring program as they relate to the capabilities of the available systems. Among the factors which should be considered in choosing a specific system are the following: the type of support provided by the system vendor, the specific data base management strategies employed by a given system, the availability of statistical and mathematical routines for data analysis, system capabilities for graphical and tabular data display, system programming capabilities, system compatibility with other available systems, and system cost.

231. The successful management of data resulting from a reservoir contaminant monitoring program will probably necessitate the combined use of both general and special purpose data base management systems. Entry of data into one of the general purpose systems shown in Table 7 would allow the resulting data to be accessed by a wide array of potential users. This would facilitate both the reservoir-specific analysis of potential contaminant problems as well as comparative analyses at regional or national levels.

232. ER 1110-2-334 specifically requires that water quality data collected at CE reservoirs should be entered into STORET; this should include data on contaminant concentrations in reservoir waters, sediments, and biota. However, available general purpose data base management systems do not provide sufficient algorithms for thorough statistical analysis of the stored data, nor is it possible to maintain rigorous quality control over data stored in a national system such as STORET. Thus, data management for reservoir-specific contaminant monitoring should also include the establishment of a localized data base, either for specific reservoirs or for a set of reservoirs under the jurisdiction of a given CE Division or District. Such a localized system should be based upon one of the special purpose systems listed in

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Table 8. Rigorous application of quality assurance procedures to data storage in a local data base would ensure access to reliable data on contaminant levels in reservoirs and would facilitate thorough statistical analysis of the data stored there. Saul et al. (1982) provide a brief discussion of the establishment of a localized data base management system for a reservoir water quality monitoring program built upon the special purpose SAS system (Table 8).

233. The key aspect of data management for a contaminant monitoring program is the careful and continual practice of quality assurance procedures in the entry of data into the chosen data base. Unless this is done, the reliability of the stored data cannot be guaranteed and the purposes for which the data were collected cannot be fully realized. Data resulting from field and laboratory analyses should be entered onto appropriately designed coding forms, and entered into the data base by keypunching or by direct entry via computer terminal.

234. The data entered should be subjected to careful point-by-point verification. The form of data entry should be consistent with considerations of the number of significant digits in the data, i.e., uncertainty should exist only in the last significant digit entered. If contaminant concentrations measured in laboratory analyses were undetectable, they should be entered into the data base as such, perhaps through the use of a specially designed code. Limits of detection should never be entered into the data base as though they were measured values. For reference purposes, the limits of detection and quantitation should be entered into the data base in conjunction with each set of data stored there (not with each individual sample entry).

235. Once the data have been entered into the data base, they should be subjected to editing programs specially designed to detect errors. Such programs should search for data formatting errors, unreasonable values (e.g., pH >14), values outside the range of expected concentrations, and other sources of likely error. The complete listing and visual inspection of individual files in the data base system may be a useful component of the data editing phase. All data entry and coding forms should be filed for future reference should questions arise

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concerning the accuracy of specific observations. Methods used to
generate specific datr should be thoroughly documented, and such written
documentation should be referenced in the data base entries and filed
for easy retrieval. Once all reasonable procedures for guaranteeing the
reliability and quality of the entered data have been taken, the data
should be transferred to mass storage devices (i.e., tape and disk) in
a manner consistent with the chosen data base management system.

236. Equally rigorous quality assurance procedures should be ap-
plied to the retrieval of contaminant data from the data base. If the
data reside on a locally designed management system, for which quality
assurance procedures are known to have been consistently applied, then
the problem of assuring the quality of retrieved data is reduced. How-
ever, for data retrieved from national general purpose systems such as
STORET, the problems of data reliability are considerable. Khalid et
al. (1983) thoroughly discuss the procedures they followed in assessing
the reliability of data retrieved from STORET. Other procedures that
can be followed will be discussed in the final section of Part VII and
in Part VIII.

237. The use of data base management systems in reservoir water
quality monitoring programs is discussed in greater detail in various
other sources. In particular, Gaugush et al. (1984) and EM 1110-2-1201
should be consulted.

Data Summarization and Preliminary Analysis

238. Once monitoring data have been entered into the data base
and thoroughly verified and edited, they should be summarized and
subjected to initial statistical analysis. This component of the over-
all data management process will facilitate the subsequent thorough sta-
tistical analysis and interpretation of results in relation to study
purposes, and will enhance communication of study results in forms use-
ful to others. The exact form in which data should be initially sum-
marized will vary according to the purposes of the specific monitoring
program, but some general suggestions can be given.

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239. Various graphic and tabular displays can be useful in reduc-
ing the total volume of data and revealing overall trends to be explored
in subsequent analyses. These displays include such techniques as fre-
quency tables or histograms and scatter plots of changes in contaminant
concentrations over time, with depth, or along longitudinal or lateral
reservoir axes. Use of such data displays can suggest the form of the
statistical distribution underlying the data of interest and thus pro-
vide information on the degree to which the data conform to assumptions
underlying the specific statistical procedures to be employed in final
data analysis and interpretation phases. Frequency tables or histograms
can be especially useful in screening the data to ensure that limits of
detection have not been entered into the data base or misidentified
during the data retrieval process as analytical measurements (Khalid et
al. 1983). The occurrence of a very high frequency of extremely low
concentration values would cause the data user to suspect that limits of
detection had indeed been entered directly into the data base or that
the retrieval process had not adequately identified such numbers.

240. Initial data summarization should also include calculation
of various basic sample descriptive statistics. Such statistics are
another means of reducing the total volume of data, providing estimates
of associated population parameters of interest, and suggesting detailed
statistical tests to be employed subsequently. Among these statistics
are the sample mean, variance and standard deviation, minimum and
maximum values, range, sample size, and various percentiles. If sug-
gested by specific data displays, it may also be useful to calculate
statistical regressions at this time, in order to explore further trends
apparent in the data.

241. The summarization and preliminary analysis of data resulting
from water quality monitoring programs is discussed in greater detail in
EM 1110-2-1201, Gaugush et al. (1984), Reckhow and Chapra (1983), and
US EPA (1982). Useful general references for summarization and statis-
tical analysis of environmental data include Box, Hunter, and Hunter
(1978), Green (1979), Mosteller and Tukey (1977), Siegel (1956),
Snedecor and Cochran (1972), Sokal and Rohlf (1979), Steel And Torrie
(1980), and Tukey (1977).

PART VIII: DATA INTERPRETATION

242. The final phase of a monitoring program involves the thorough statistical analysis of the resulting data and the interpretation of analytical results in relation to study purposes and management needs. The purpose of monitoring is to support the management of reservoirs and other water resources. Thus, interpretation of monitoring data must lead to unambiguous results which can be translated into feasible management options for reducing the severity of any contaminant problems discovered during the course of the monitoring program. Although the success of the data interpretation phase will be enhanced by a well-designed sampling program based upon specific and clearly stated goals, the translation of study results into feasible management options is a difficult process (Ballinger 1979, Briggs 1979, Khalid, et al. 1983, Mills et al. 1982, Rice and Anderson 1979).

243. Data available for selecting and evaluating management options are frequently inadequate or of the wrong type. Moreover, delineation of feasible management approaches requires considerable supporting information and data on contaminant sources and properties and on the environmental behavior of contaminants of concern. Finally, options available for minimizing the severity of reservoir contaminant problems may be quite constrained. Reservoir contamination is a general watershed problem, and available management options may be severely limited if contaminant loadings to a reservoir cannot be controlled.

244. For the data interpretation phase to yield defensible results, monitoring data must have resulted from a statistically sound and well-executed sampling program. All data base management procedures must have been carried out in such a manner that careful attention has been given to the reliability and quality of the resulting data. Initial screening and summarization of the data base, as well as preliminary statistical analysis, should have preceded thorough analysis and interpretation. The specific analyses to be performed during the data interpretation phase will be dictated by the stated purposes and objectives of the monitoring program. In general, the goal of this phase

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will be to determine whether contaminant problems exist in a reservoir, as well as to identify any nonrandom trends in water quality conditions in the reservoir under study (e.g., such as might result from the application of certain management procedures designed to reduce a previously identified contaminant problem).

245. A subsidiary goal of the data interpretation phase might be to analyze accessory hydrologic and water quality data so as to understand basic physical, chemical, and biological processes which regulate contaminant behavior in the reservoir in question, and thereby to identify likely management options for mitigating any existing contaminant problems. Although identification of potential contaminant impacts on biological populations within the reservoir might be an important consideration in many circumstances, it is beyond the scope of this report and will not be considered here.

246. The primary focus of the material which follows is the interpretation of data resulting from a specific monitoring program designed to detect the occurrence of contaminants in a single reservoir. However, it must be recognized that the screening of reservoirs for possible contaminants may require the analysis and interpretation of data collected for diverse purposes and/or derived from many sources. For example, data drawn from a national water quality data base (e.g., STORET) may be used as part of a preliminary screening to decide whether field monitoring is required. Similarly, data resulting from a limited sampling program may be analyzed to determine the effects of some management technique applied to minimize the presence of known contaminants.

247. Where the data to be analyzed have resulted from a reservoir-specific monitoring program and have been stored in a local data base, and where rigorous quality assurance procedures have been carefully followed throughout, potential problems in data interpretation will be minimized. However, where data have been drawn from other sources, they must be analyzed and interpreted carefully in relation to unknown problems which may be masked in the data base. Thus, the discussions which follow provide a thorough basis for interpreting data on

contaminant levels in reservoir waters, sediments, and biota, whether the data have resulted from a carefully designed, reservoir-specific monitoring program or not.

248. The following section discusses the potential problems in interpreting the mass of information included in a water quality data base. The next section reviews basic concepts of statistics and probability theory that must be considered in interpreting contaminant data in relation to existing water quality criteria and standards. The third section following reviews these criteria and standards and discusses how they should be used together with monitoring data to decide whether contaminant problems exist in a given reservoir. Next, the use of available screening methods to manage reservoirs in relation to potential contaminant problems is discussed. The final section considers the specification and evaluation of management options for minimizing contaminant problems discovered during a monitoring program.

Potential Problems in Data Interpretation

249. As suggested above, it may be necessary to interpret data derived from a variety of sources during the course of a reservoir monitoring program. Not all of these data may have been collected or entered into the water quality data base of interest in a manner that ensures the quality and reliability of the data or the conclusions drawn from them. The potential user needs to be aware of problems which can be masked in such data, so that he can avoid reaching false and unsupportable conclusions based upon his data analyses.

250. Some problems that may be hidden in a reservoir contaminants data base are of a fairly general nature, and are common to many large-scale water quality monitoring networks (Ballinger 1979, Briggs 1979, Rice and Anderson 1979, Sanders and Ward 1979, Wolman 1971). These include problems associated with the general paucity of data, short record lengths, changes during the course of the monitoring program in sampling location and frequency, unavailability of useful accessory data on hydrologic and general water quality conditions, data collected in a

haphazard fashion, and lack of information on data variability in time and/or space. Most of these problems are symptomatic of a poorly designed field monitoring effort; little can be done to correct for them during the data interpretation phase. Other, more specific problems exist, however, which can be avoided if data analyses are carefully applied and interpreted.

251. One such problem concerns the entry of limits of detection into the data base as though they were actual analytical readings (Khalid et al. 1983). Careful data screening and preliminary analysis should detect the occurrence of such problems. If not, however, false conclusions can be reached, particularly if the prevailing limit of detection for a particular chemical contaminant is larger than the critical concentration specified in relevant criteria and standards. In such cases, uncritical interpretation of data analyses would lead to the possibly false conclusion that a water quality problem exists in the sampled reservoir. Instead, the only reasonable interpretation in such instances (in the absence of additional supporting data) would be that one cannot ascertain with certainty whether or not a water quality problem exists in the reservoir in question without further monitoring using more sensitive analytical methods.

252. Another data base problem that could lead to improper conclusions concerns changes over time in the analytical methods employed in a monitoring program, especially if the various methodologies have not been carefully cross-calibrated (Khalid et al. 1983, Shapiro and Swain 1983). In the absence of specific information on the comparability of data derived from the several methods, false conclusions concerning trends apparent in the contaminants data could be reached. This problem could be particularly acute if combined with the one just discussed, i.e., if limits of detection have been entered directly into the data base without being identified as such, and these limits have decreased in magnitude due to improvements in analytical methods. In this instance, uncritical interpretation of trends in the data base would incorrectly suggest that water quality conditions had improved over time, when all that had really occurred was a lowering of the minimum

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detectable concentration of the chemical contaminant of interest. Shapiro and Swain (1983) provide a particularly instructive example of problems that can result from changes in analytical methods (and in contracting laboratories) over long periods of time in water quality monitoring programs.

253. Another potential data interpretation problem that could lead to false conclusions stems from the incorrect comparison of monitoring data with the relevant water quality criteria and standards (Khalid et al. 1983, Rice and Anderson 1979). These criteria and standards reflect the best available scientific information on the maximum tolerable exposures to toxic chemicals for human and aquatic populations. Typically, these critical concentrations were derived from laboratory bioassays in which organisms were exposed to known concentrations of the contaminant of interest in water-soluble form. Thus, monitoring data for comparison with these standards should reflect analyses of filtered rather than bulk or unfiltered samples. The actual dissolved concentration of a given contaminant in unfiltered water samples may depend largely on the concentration of suspended sediments in the sample, which may be unknown and may vary considerably from sample to sample. Thus, comparison of concentrations measured on unfiltered samples with existing criteria and standards could lead to erroneous conclusions concerning the presence or absence of contaminant problems in a given reservoir.

254. A final problem that must be considered during data interpretation concerns a basic incompatibility between water quality criteria and standards and field monitoring data (Loftis, Ward, and Smillie 1983; Sanders and Ward 1979). As they are typically written, standards represent fixed upper limits that are not to be exceeded by concentrations measured during a monitoring program. In comparison, monitoring data represent samples drawn from some parent population about which information is desired. By its very nature, sampling is a statistical process. There exists a finite possibility that a measured concentration could exceed a fixed standard due strictly to natural variability or sampling error. Similarly, trends in field monitoring data could

reflect random variation or natural cycles rather than real trends
for improvement or deterioration of water quality associated with an-
thropogenic impacts. Thus, data analysis and interpretation must be
able to distinguish actual water quality trends from apparent trends
resulting from sampling error and natural variability in time and space.
This involves the use of statistical methods and concepts from probabil-
ity theory during the data interpretation phase. The following section
summarizes basic statistical and probability concepts which should be
considered in comparing monitoring data with relevant standards.

Statistical Considerations

Statistical approaches to data interpretation

255. At the end of a monitoring program, after all field data
have been screened and entered into the data base, one may be tempted
simply to scan the resulting data, locate the maximum concentration ob-
served, and conclude based upon a comparison of this concentration with
the relevant water quality standard that a contaminant problem either
does (maximum concentration > standard) or does not (maximum concentra-
tion < standard) exist in the sampled reservoir. The same procedure
could be repeated for all of the contaminants measured during the course
of the monitoring program. Although this procedure seems straightfor-
ward and is easy to apply and interpret, it fails ( ) to take into
account the statistical nature of monitoring data and (b) to distinguish
clearly the actual degradation of water quality due to anthropogenic
impacts from random and/or cyclical variations in contaminant concentra-
tions which are unrelated to human impacts on water quality conditions
in the sampled reservoir. Thus, alternative procedures based on appro-
priately applied statistical concepts should be employed to interpret
monitoring data in relation to existing criteria and standards (Briggs
1979; Erlebach 1979; Loftis, Ward, and Smillie 1983; Rice and Anderson
1979; Sanders and Ward 1979).

256. To better understand the discussions which follow, consider Figure 1. Assume that the concentration of some specific chemical

AREA REPRESENTS THE PROBABILITY OF EXCEEDING THE RELEVANT WATER QUALITY STANDARD, Xs
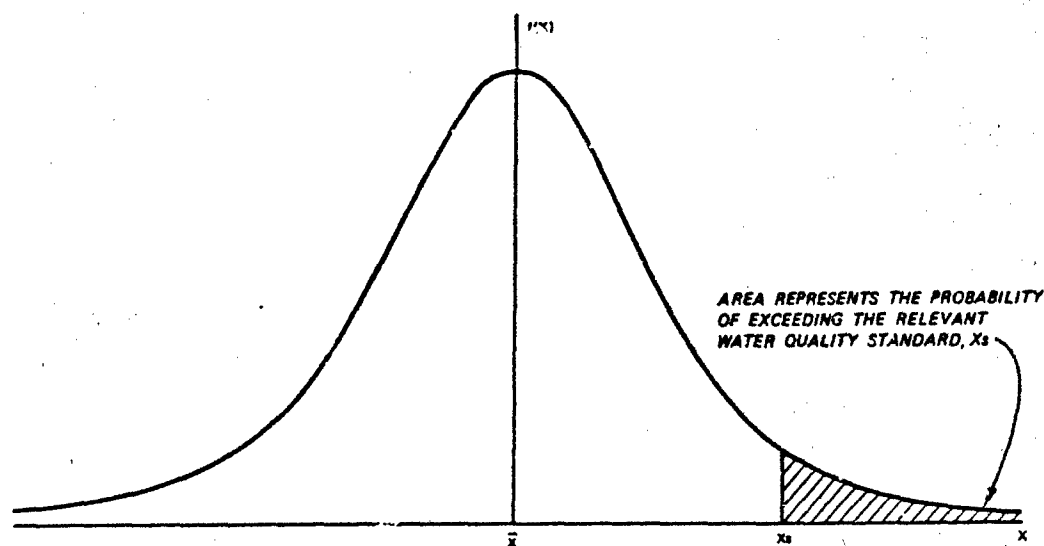
Figure 1. Representation of the probability distribution f(X) of sample values for concentrations of a specific contaminant in random water samples from a given reservoir; X̄ represents the observed sample mean and Xc represents the relevant water quality standard for this chemical

contaminant of interest follows a normal distribution (any other distribution could serve as an example), and that randomly located samples of water have been collected from a specific reservoir and properly analyzed for contaminant concentrations. Various sample descriptive statistics are calculated as point estimates of the unknown population parameters: the true population mean is estimated by the sample mean ($\bar{X}$), and the dispersion of values around the mean is represented by the sample variance (s^2), standard deviation (s), and standard error of the mean ($s_{\bar{X}}$). For this normal population, the problem is to determine, based strictly on the sample values, whether or not the reservoir is in violation of a specific standard, represented by Xs in Figure 1. Even if $\bar{X}$ < Xs as depicted, there exists a finite probability that a single randomly drawn sample, or the mean of a randomly drawn sample population, will exceed the relevant standard due strictly to sample error or

natural variability, regardless of whether a water quality problem
exists or not. This probability is not clearly related to whether or
not one or more concentrations in the original sample exceed Xs .
Thus, data interpretation must be able to distinguish "real" water qual-
ity violations from apparent violations resulting strictly from the sam-
pling process. Because of this, data analysis and interpretation must
relate monitoring data to relevant water quality criteria and standards
through the use of sampling statistics (Loftis, Ward, and Smillie 1983;
Sanders and Ward 1979).

257. In this instance, a concentration specified in an appropri-
ate water quality standard is no longer interpreted as a fixed upper
limit never to be exceeded, but rather as an upper limit not to be ex-
ceeded some specified percentage (e.g., 95 or 99 percent) of the time.
This specified percentage represents the fraction of the total area
under the probability distribution of sample concentrations $f(X)$,
lying to the right of the standard Xs (Figure 1).

258. In taking a statistical approach to the interpretation of
monitoring data, one must assume that the underlying sampling program
was properly designed and executed. That is, sample size must be suf-
ficiently large to estimate population parameters of interest with rea-
sonable confidence; samples must have been drawn randomly, if not from
the entire reservoir then from essentially homogeneous strata; and sam-
pling frequency must be sufficiently great to provide reliable informa-
tion on natural temporal variability in contaminant concentrations.
This last point is critical: knowledge of data variability in time and
space is essential to the proper interpretation of monitoring data on
contaminant levels in reservoirs in relation to standards and criteria
(Ballinger 1979, Briggs 1979, Erlebach 1979, Rice and Anderson 1979,
Sanders and Ward 1979). Also, knowledge of the possible environmental
behavior of the contaminant(s) of interest must have been taken into
account in designing the field sampling effort, and must be considered
in interpreting monitoring results (Khalid et al. 1983, Milis et al.
1982).

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259. A number of statistical possibilities for interpreting monitoring data must be considered (Loftis, Ward, and Smillie 1983; Sanders and Ward 1979). On the one hand, the data user may want to determine whether or not the sampled reservoir is in compliance with existing water quality criteria and standards. Alternatively, one may be interested in identifying trends in the data base which reflect an improvement or degradation of water quality conditions in the reservoir under study. Finally, interest may focus on examining relationships between contaminant concentrations and hydrologic or other water quality variables. Identification of such relationships may reveal key processes regulating the environmental behavior of the contaminants of interest, and may suggest management techniques for mitigating any contaminant problems detected. Each purpose for data interpretation will require a different statistical treatment of the available data. Statistical approaches useful for each of these three general purposes will be briefly discussed.

Detection of water quality violations

260. Determining whether or not a sampled reservoir is in violation of existing standards involves the use of statistical inference, i.e., testing the hypothesis that a single random sample exceeds the standard ($X > Xs$), or that the mean of a random sample population exceeds the standard ($\bar{X} > Xs$). If one is testing an hypothesis involving a single random sample, then one uses the sample standard deviation in the appropriate statistical calculations. By contrast, hypotheses involving the mean of a random sample population require the use of the standard error of the sample mean. As discussed later, which hypothesis one tests depends on the nature of the relevant standard.

261. A number of legitimate statistical approaches exist for testing such hypotheses. In order to illustrate the procedure involved, data on two hypothetical populations have been generated and are summarized in Table 9. These hypothetical data could represent the concentration of any contaminant in any environmental compartment sampled (i.e., water, sediment, tissue); for the purposes here, assume they

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represent concentrations in (filtered) water samples in units of micro-grams per litre. These readings might have resulted from a biweekly sampling of water from a single homogeneous stratum of a reservoir, or (preferably) an equivalent number of samples collected on an event-oriented basis. For this example, let the relevant standard be 100 µg/ℓ.

261. These hypothetical data are fairly typical of the sample readings one might expect in a field sampling program. Each of the two sample data sets contains a number of zero readings, and both contain one or more concentrations in excess of the standard. In the first sample population, only a single value is slightly larger than the standard; in the second, 12 of 26 values exceed the standard, often quite substantially. Means of both hypothetical populations are less than the standard, and the variation of sample values around each mean is quite large (the coefficient of variation was chosen at about 0.75-0.80 for each population). Thus, an initial scan of the two data sets might suggest that a reservoir from which the first sample was collected is not in violation of the stated standard (even though the maximum value does exceed the standard), while a reservoir from which the second sample was taken is in violation. Several statistical techniques exist for attaching specific probability statements to these initial impressions.

262. One valid approach to making initial impressions concerning these two populations quantitative is the calculation of appropriate confidence intervals. Since one is only interested in whether or not sample values exceed the standard, the one-tail upper confidence limit is the quantity to calculate. For the first population in Table 10, the upper 95-percent confidence limit on a single randomly chosen sample value is 94 µg/ℓ. Similarly, the upper 95-percent confidence limit on the mean of a random sample population is 51 µg/ℓ. (The first confidence limit is calculated using the appropriate value from the Student's t distribution and the sample standard deviation; the second limit is calculated with the same t value but the standard error of the sample mean. Since the standard deviation is always larger than the standard error, the first upper confidence limit will always be larger

than the second. Statistically, this simply says that there is always more uncertainty in the magnitude of a single sample value than in the mean of a set of sample values, a restatement of the Central Limit Theorem from probability theory.) Comparable upper confidence limits for the second population in Table 9 and 186 and 101 µg/ℓ, respectively. Both of the upper confidence limits for the first population are less than the standard of 100 µg/ℓ, while both values for the second population exceed this standard. Using a higher level of probability (e.g., 99 percent) would raise all upper limits, while the reverse would be true if lower probability levels were chosen.

264. A second approach is to test whether the reservoir in question is in violation through the use of the standard normal distribution. In this case, the stated water quality standard is converted to a standard normal variate by subtracting the observed sample mean and then dividing by the sample standard deviation or the standard error. One then determines the associated probability level by looking up this value in a table of the cumulative standard normal distribution. For the first population in Table 9, the probabilities that a single random sample or the mean of a random sample population will exceed the standard based on this approach are 0.030 and 0.0, respectively. Comparable values for the second population are 0.378 and 0.056. As did the upper confidence limits, these values tend to confirm the initial impression that the first reservoir is not in violation of the standards, while the second is.

265. Because the above probability values are based on sample estimates of the standard deviation and standard error, there is a certain amount of uncertainty associated with them. Loftis, Ward, and Smillie (1983) discuss how to place confidence bounds around such probability statements based on the standard normal distribution. An alternative procedure is simply to use the Student's t distribution instead of the standard normal. Using this distribution for the first hypothetical population, the probabilities that a single random sample or the mean of a random sample population will exceed the standard are 0.038 and 0.0, respectively. Comparable values for the second population are

0.380 and 0.065. These values are quite similar to those based on the standard normal, but slightly larger since the true population variance is unknown.

266. All of these methods represent valid applications of sampling statistics to the comparison of monitoring data with water quality criteria and standards. In order to use them properly, the user must make two decisions. First, one must determine whether he is interested in the probability that a single random sample value exceeds the standard, or the probability that the mean of a random sample population exceeds the standard. In general, if the standard is stated in the form of a maximum value not to be exceeded (i.e., corresponding to an acute toxic effect), then it is the probability that a single random sample value will exceed the standard that should be calculated. Alternatively, if the standard is stated as some type of average value (e.g., a 24-hr average) not to be exceeded (i.e., corresponding to a chronic effect), then it is the probability that the mean of a random sample population will exceed the standard that should be determined. Second, one must decide what probability level to adopt as the criterion for violation. Where the consequences of exceeding the standard for the health of human and aquatic populations are great, and/or the scientific basis of the standard is somewhat uncertain, a higher probability criterion should be adopted (e.g., 95 or 99 percent). On the other hand, if exceeding the standard does not pose extreme risk for human or aquatic populations, and/or the scientific basis for the existing standard is quite certain, then somewhat lower probability levels could be chosen (e.g., 80 or 90 percent).

267. The appropriate probability level will differ among contaminants and reservoirs depending on many study-specific factors. Wherever there is real uncertainty as to the appropriate level, one should always choose a high enough level to ensure the safety of human and aquatic populations likely to be impacted by any contaminant problems in the reservoir in question. Choice of a higher probability means that a smaller mean concentration is required to conclude that a reservoir is not in compliance with existing criteria and standards. In

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statistical terms, the higher the probability level chosen, the smaller is the chance of concluding erroneously that no contaminant problems exist in a given reservoir when in fact some do (i.e., accepting a false null hypothesis or making a so-called Type II error).

268. A slightly different approach to detecting standards violations was developed by Loftis, Ward, Smillie (1983), and Sanders and Ward (1979). Their approach involves calculating the number of violations expected during the course of a field monitoring program. This expected value is calculated as the product of the sample size and the probability of exceeding the standard. If the observed number of violations is greater than the expected number, one would conclude that a water quality problem existed. This approach has merit for detecting violations of standards for conventional pollutants, particularly in streams and rivers. However, it contains a number of hidden assumptions, and could lead to serious errors in judgment for detecting problems with toxic pollutants in reservoirs. In particular, the approach implicitly assumes that the probability of exceeding the standard can be calculated based upon a sample from a time period known not to be impacted by human activities. The original references should be consulted carefully for a complete discussion of the approach.

269. All of the statistical methods discussed here for detecting violations of standards for toxic chemicals in reservoirs are based upon certain specific assumptions (e.g., the variable in question follows a specific distribution, such as the normal or lognormal). Thus, as part of the data interpretation phase, the validity of these underlying assumptions should be carefully evaluated. This involves other statistical procedures such as goodness-of-fit tests. If the available data on contaminant concentrations in reservoirs do not conform to these assumptions, other nonparametric or distribution-free statistical methods should be employed. Nonetheless, in determining whether or not the sampled reservoir is in compliance with existing water quality criteria and standards, it is preferable to use statistical methods based on reasonable assumptions than not to follow a statistical approach at all (Loftis, Ward, and Smillie 1983; Sanders and Ward 1979).

Detection of water quality trends

270. A second general purpose for analyzing monitoring data involves identification of nonrandom trends. One might be interested in changes in reservoir contaminant levels due to changes in industrial activities or agricultural practices in the contributing watershed. Alternatively, one may wish to determine whether some management procedure was leading to a reduction of contaminant concentrations within the reservoir. Or, one could be interested in examining spatial gradients in contaminant concentrations along horizontal or vertical reservoir axes. Data on contaminant levels in samples of water, sediment, or biological tissues could be analyzed for the detection of trends for any one of these purposes.

271. A number of statistical approaches exist for detecting trends in water quality data. Perhaps the simplest involves the calculation of linear or nonlinear regressions of changes in contaminant concentrations in time or space. Such regression analyses will detect whether the apparent trend is statistically significant or not, as well as predict the rate at which contaminant concentrations are changing. More sophisticated methods of trend detection, involving procedures from time series analysis and statistical filtering, are also possible.

272. Another approach to detecting trends in reservoir contaminant concentrations involves testing specific statistical hypotheses concerning changes in mean concentrations in time or space. For example, data on contaminant concentrations before and after the implementation of some specific management procedure might be subjected to a two-sample (pooled) t-test to detect the significance of observed changes in contaminant concentrations attributable to reservoir management.

273. The hypothetical data in Table 9 again serve to illustrate the procedure involved. Data for population 2 could represent water concentrations prior to implementation of the management approach, while population 1 data could represent postmanagement conditions. On the assumption that no other changes in the reservoir or the watershed have occurred, these data suggest that the specific management approach employed led to a reduction in concentration of this hypothetical

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contaminant of 41 µg/l. For these data, the pooled estimate of variance is 2397 µg/l, the estimated standard error of the difference in mean concentrations is 14 µg/l, and the calculated t value is 2.98; the associated probability level is about 0.007. One would conclude from this analysis that contaminant levels had indeed been reduced by the management method employed.

274. The statistical approach just illustrated can be expanded to more than two time periods through the use of analysis of variance techniques. With these techniques, one can partition the total variation in the data set into both temporal and spatial components, and test for the significance of the observed trends in time and/or space as desired. Thus, for example, one could examine the significance of measured differences in contaminant concentrations among several spatial strata over two or more time periods in a single analysis. How one specifically employs such statistical methods for detecting differences in concentrations in time and/or space will be determined by the design of the field sampling program.

Identification of
water quality relationships

275. The third general purpose previously identified for analyzing and interpreting contaminant monitoring data involves examining relationships between contaminant concentrations and hydrologic and other general water quality variables. For example, one might examine relationships between contaminant concentrations and total tributary flow into the reservoir, or between contaminant concentrations and concentrations of suspended sediments. Data on other water quality variables to be used in such analyses might be drawn from a variety of sources, including CE Division water quality surveys on specific reservoirs, studies by local universities or state or other Federal agencies, or national water quality data bases such as STORET and WATSTORE. Another excellent source of such data is an extensive data base on water quality conditions in CE reservoirs described by Walker (1981, 1982, 1984).

276. Various statistical procedures exist for examining relation-ships between contaminant concentrations and other water quality vari-ables. These include the fitting of various linear and nonlinear regression models of assumed relationships between contaminant concen-trations and other variables which are believed to regulate the behavior of the contaminants of interest in the sampled reservoir. Alterna-tively, one could examine relationships between contaminant and other water quality variables through the use of statistical correlation pro-cedures. Both simple univariate and multivariate partial and canonical correlation analyses could prove useful, depending on study purposes and field sampling design. Again, the main intent of such statistical ana-lyses is to identify relationships between contaminant and other vari-ables, and thereby hopefully to identify key processes which appear to be regulating the environmental behavior of the contaminants of inter-est. Understanding such key regulatory processes might suggest management approaches useful for mitigating any reservoir contaminant problems detected.

Other sources of information

277. The purpose of this section has been to stress the impor-tance of adopting a rigorous statistical approach to analyzing and interpreting data on reservoir contaminant levels resulting from a moni-toring program, and to illustrate the types of approaches that may be employed. For detailed discussion of appropriate statistical methods, the reader is directed to the following references: EM 1110-2-1201; Gaugush et al. (1984); Box and Jenkins (1976); Box, Hunter, and Hunter (1978); Draper and Smith (1981); Green (1979); Morrison (1976); Mosteller and Tukey (1977); Parzen (1960); Reckhow and Chapra (1983); Siegel (1956); Snedecor and Cochran (1972); Sokal and Rohlf (1979); Steel and Torrie (1980); Tukey (1977); and US EPA (1982).

Compliance with Regulatory Criteria and Standards

278. The major purpose for analyzing data on contaminant concen-trations in reservoir water, sediments, and biota--whether these data

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were derived from a reservoir-specific monitoring program or from some
general water quality data base—is to determine whether or not a spe-
cific reservoir is in compliance with existing water quality criteria
and standards. Successful realization of this purpose requires (a) that
the data user is thoroughly familiar with the statistical considerations
discussed in the previous section and (b) that he is aware of the rele-
vant criteria and standards and knows how to employ them to identify
problem reservoirs. The intent of this section is to review briefly the
available criteria and standards and to provide general guidance on how
and when to use them to determine if a given reservoir does or does not
comply with them. The statutory basis and general content of the rele-
vant criteria and standards were summarized in Part I of this report;
Part II listed the various chemical contaminants covered by these regu-
lations. The actual concentration levels specified by these regulations
may be found in summary tables in the reservoir contaminant survey by
Khalid et al. (1983) and in the original sources cited therein.

279. The following criteria and standards are available for com-
parison with data on contaminant concentrations in reservoir water sam-
ples: the EPA 1980 and 1976 Red Book criteria, the PHS National Drink-
ing Water Standards, and state water quality standards. The EPA 1980
criteria, based on the best scientific information currently available,
specify maximum concentrations for the protection of human health and
aquatic life. The human health criteria are stated in the form of maxi-
mum concentrations not to be exceeded, while the criteria for aquatic
life specify both a 24-hr average and an absolute maximum concentration
not be to exceeded. These two aquatic life criteria correspond to
chronic and acute toxic effects, respectively. Based on improved
scientific information, these criteria supplanted the earlier 1976 cri-
teria, which also specified separate levels for the protection of human
health and aquatic life. The 1976 criteria did not, however, specify
separate average and maximum criteria for aquatic life. The concentra-
tions for aquatic life specified in the 1976 criteria generally fall
between the two levels specified in the newer 1980 criteria.

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280. These EPA criteria do not by themselves have any regulatory impact, unless they are incorporated into state water quality standards, which are enforced. Most current state standards are based on the 1976 criteria, although a gradual transition to the newer 1980 criteria is in progress. The PHS Drinking Water Standards differ from the EPA criteria since they take into account economic and technical feasibility of compliance (the EPA criteria do not consider such factors), and since they are based upon a different risk model. They are also stated in the form of maximum concentrations not to be exceeded.

281. Which of the available criteria and standards one utilizes to detect the presence of contaminant problems in a given reservoir will depend on the purposes for which the monitoring data were collected. In general, since they may reflect local considerations not covered in national criteria, one should base decisions concerning compliance on the relevant standards for the state in which the reservoir is located. However, if the state standards are still based on the older EPA 1976 Red Book criteria, one should strongly consider using the newer, more scientifically sound 1980 criteria, especially if they differ substantially from the 1976 criteria and/or the relevant state standards. For the few chemicals listed in Tables 2 and 3 not covered by the 1980 criteria, state standards or the 1976 criteria should be followed.

282. If the purpose of data interpretation is to derive information at a national or regional level on the occurrence of contaminant problems in a variety of CE reservoirs (e.g., all reservoirs in a Division, all CE reservoirs), then the 1980 criteria should certainly be employed. Unless there exists strong scientific evidence to the contrary, one should probably employ the most stringent standard available, so as to provide maximum possible protection to human and aquatic populations likely to be impacted by the occurrence of any reservoir contaminant problems.

283. Whichever set of standards is chosen as the basis for interpreting data on water-soluble concentrations of the contaminants of interest, proper statistical procedures should be employed for comparing the standard with field monitoring data. As already emphasized, if the

standard is stated as an absolute maximum concentration not to be exceeded (e.g., the 1980 EPA criteria for the protection of human health), then decisions concerning reservoir compliance should be based on the calculated probability that a single random sample will exceed the standard. In contrast, if the standard is stated in the form of an average concentration not to be exceeded (e.g., the 1980 EPA criteria for the protection of aquatic life from chronic effects), then compliance decisions should be based on the calculated probability that the mean of a random sample population will exceed the standard.

284. For data on contaminant concentrations in tissue samples from finfish and shellfish species ingested by human populations, the relevant standards are provided by the FDA regulations on maximum concentrations of contaminants in aquatic organisms. Since these regulations are stated in the form of maximum concentrations not to be exceeded, the decision as to whether or not contaminant problems exist in the sampled reservoir should be based on the calculated probability that a single random sample will exceed the stated standard.

285. For other types of samples not covered by these standards, it is possible to calculate and use various derived standards for the purpose of deciding whether or not a potential contaminant problem appears to exist in the sampled reservoir. For example, for sediment concentrations, tentative standards can be calculated based on the appropriate water-soluble standard and theoretical considerations concerning the equilibrium partitioning of the contaminant in question between sediment and water (i.e., derived standard equals water standard multiplied by equilibrium partition coefficient).

286. Similarly, a sediment standard could be derived from an FDA tissue standard with knowledge of the equilibrium bioconcentration of that contaminant from sediment by an appropriate finfish or shellfish species. Such derived standards are also possible for various aquatic species not directly covered by the FDA regulations, based on knowledge of the relevant water-soluble standard and the bioconcentration factor of that chemical from water by the species in question. Such approaches

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are discussed in a number of other sources (e.g., Khalid et al. 1983; Lyman, Reehl, and Rosenblatt 1983; Mills et al. 1982).

287. Although many such derived standards may be calculated, they should be used and interpreted with extreme caution. Such derived standards have an uncertain legal basis, and many scientific objections exist to using constant values for partition and bioconcentration coefficients. Such coefficients are known to vary considerably as a function of many physical, chemical, and biological factors. Thus, although these approaches to calculating derived standards may be useful in certain well-defined situations, the user should be aware of the many pitfalls and assumptions involved. The use of derived standards is currently receiving considerable attention, and more definitive guidance may be available in the future.

288. The specifics of data comparison with water quality criteria and standards will be dictated by the detailed purposes of a given monitoring program. Also, the criteria and standards may themselves change over time, as new laws are enacted and as the scientific basis of water quality regulation improves.

Use of Screening Methods in Reservoir Management

Need for screening methods

289. After the monitoring data have been analyzed and compared with appropriate criteria and standards in a statistically rigorous manner, a decision must be reached concerning the proper future management of the reservoir under study. If a contaminant problem has been detected, management options for minimizing adverse environmental impacts resulting from the problem must be identified and evaluated as to their cost and likely success. If no contaminant problem has been detected, then it may still be necessary to schedule a reevaluation at some future date in relation to projected changes in human impacts on the reservoir. In either case, reliable techniques for translating monitoring results into feasible management options must be employed.

290. As compared with the case for more conventional pollutants, the management of reservoirs in relation to the occurrence of toxic pollutants is more difficult; the environmental controls required to minimize adverse environmental impacts are more costly; and the penalties—in terms of adverse impacts on the health of human and aquatic populations—for errors in judgment are more severe (Mills et al. 1982). Thus, the translation of monitoring results into management options requires the use of efficient tools that are based on thorough knowledge of key processes regulating the environmental behavior of toxic contaminants, both organic and inorganic.

291. One particularly useful set of tools for translating monitoring results into management options is contained in a set of screening procedures published by the EPA for assessing the environmental quality of aquatic environments including reservoirs (Mills et al. 1982). Part II of this report briefly reviewed the use of these screening procedures in relation to the selection of variables to be included in a contaminant monitoring program. These methods, which combine empirical and mechanistic approaches applicable to both conventional and toxic pollutants, were designed to provide a rapid assessment of the presence of pollution problems in water bodies, as well as an evaluation of management options for mitigating any problems identified.

292. Recognizing that water pollution is a watershed-level problem, these methods focus on factors that influence the inputs of pollutants to water bodies, as well as those that regulate the behavior of pollutants within aquatic ecosystems. The primary output of the methods is a prediction of pollutant concentration in the water body in question, with a secondary output for reservoirs being the concentration of pollutants of interest in tissues of aquatic organisms, primarily fish. Thus, these methods are similar in spirit to commonly used loading or regression models for predicting the eutrophication potential of lakes and impoundments (e.g., Reckhow and Chapra 1983, Walker 1982).

293. The content and use of these screening procedures in relation to the management of contaminant problems in reservoirs will be summarized in the paragraphs which follow. Detailed descriptions of the

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individual methods, including numerous example calculations, may be found in the manual prepared by Mills et al. (1982). This manual also contains a wealth of background information on the properties, sources, and environmental behavior of contaminants essential to intelligent application of the screening procedures.

294. As background information to the discussion of the proper use of the screening procedures for managing contaminant problems in reservoirs, the following paragraphs present a review of the technical content and concepts of the procedures.

Screening methods

295. The individual screening methods developed by Mills et al. (1982) are based on a general screening procedure that can be adapted for specific application to three types of aquatic environment: river, impoundment, and estuary. Methods appropriate for each environment can be used separately, or the methods can be used in an interactive manner to provide an integrated analysis of aquatic systems interconnected by flows. Although the methods specifically developed for impoundments are of immediate concern here, the riverine techniques may also prove useful for assessing contaminant problems in reservoirs. These riverine methods may be applied directly to shallow, unstratified impoundments, or they may provide a means of assessing contaminant loadings to reservoirs from upstream sources. Also, the riverine methods provide a mechanism of analyzing the fate and impacts of contaminant spills on reservoirs, thus providing the "quick response capability" identified by Khalid et al. (1983) as missing from existing contaminant monitoring programs for reservoirs. Mills et al. (1982) provide two examples of analyzing the fate and transport of a toxic chemical spilled into a river, for toxicants that are both less and more dense than river water.

296. These screening methods are based on the conceptualization of major processes regulating the environmental behavior of contaminants. As shown in Table 10, up to 13 processes in four major categories which influence contaminant fate and transport in aquatic environments may be considered in a given analysis. All of these processes are potentially important for understanding the behavior of organic

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contaminants; some, however, do not apply to the analysis of metals (e.g., photolysis). The effect of each of these processes on contaminant concentrations in the water body of interest is formulated in terms of first-order kinetics. Application of the resulting equations allows prediction of the steady-state concentration of a given contaminant, calculated as the concentration in the inflow to the reservoir divided by the quantity one plus the product of the water residence time and the composite loss or turnover rate. This composite turnover rate is in turn calculated as the summed rates of loss from each of the processes listed in Table 10, which is felt to exert a significant enough influence on the contaminant under investigation to be included in the analysis.

297.   In order to use the techniques intelligently, one must have thorough understanding of the specific processes affecting the environmental behavior of a given contaminant in the reservoir of interest, as well as of the likely sources and relevant chemical properties of that contaminant. Mills et al. (1982) provide extensive background information on these topics. Other useful references for information on contaminant properties, sources, and environmental behavior include Callahan et al. (1979); Khalid et al. (1983); Lyman, Reehl, and Rosenblatt (1982); Stumm and Morgan (1981); Tinsley (1979); and Verschueren (1983).

298.   Once the specific processes to be included in a given analysis are identified, application of the actual screening methods proceeds in a sequential manner. Three different levels of analysis are possible for predicting the water-soluble concentration of the contaminant under consideration (Table 10). Each successive level provides a more realistic prediction of the steady-state contaminant concentration; involves fewer simplifying assumptions concerning the processes influencing the environmental behavior of that contaminant; and requires more information on contaminant properties and rate coefficients.

299.   After calculations at each level have been completed, the predicted concentration is compared either with existing water quality criteria and standards or with measured concentrations, to determine if

that level of analysis either suggests the presence of a contaminant problem or explains the observed results. If no contaminant problem is detected at a given level, or if the predicted concentration agrees well with observed values, then the analysis terminates at that step. Otherwise, the procedure continues on to the next, more refined level of analysis.

300. The first level of analysis involves treating the contaminant of interest as a conservative substance (Table 10). That is, only contaminant additions to and losses from the reservoir associated with flows are considered; no internal reactions are included in first-level calculations. In terms of comparing the predicted concentration with water quality standards, this level provides the worst-case analysis, i.e., the highest predicted concentration. For this level of analysis, no data are required on internal reaction rates; only information on estimated loads and flows are required. This level will overpredict the contaminant concentration at steady state if other than strictly advective processes are affecting contaminant dynamics, but it will also underpredict the duration of contaminant exposure since it does not consider contaminant releases to the water column from sediments.

301. The second level of analysis specified in the screening procedures adds consideration of other transport and speciation processes to the first-level analysis (Table 10). Thus, this second level focuses on all processes which affect contaminant removal from the water column or transport out of the water body. It does not include consideration of processes which transform the contaminant in question. This level represents a relatively straightforward refinement of the first-level analysis. Additional data required for this level are generally readily available or estimable from known chemical properties of a given contaminant. The steady-state contaminant concentration predicted at this level will be lower than at the first level since various loss processes considered here were ignored in first-level calculations.

302. The third level of analysis completes the consideration of contaminant dynamics within the water column by including those processes which affect contaminant transformation to other forms which may

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or may not be toxic, depending on the chemical under study. Again, most of the new data required at this third level are estimable from known chemical properties. As was the case in the transition from the first-to the second-analysis level, the predicted contaminant concentration at steady state will be lower at this level since additional contaminant loss processes not considered at previous levels are included here.

303. Although not identified as such in the screening procedures (Mills et al. 1982), a fourth level of analysis is required to predict the accumulation of contaminants in tissues of aquatic organisms (Table 10). The screening methods specifically include techniques for predicting the direct concentration of contaminants from water through the use of bioconcentration factors.

304. The specific application of the general screening approach described above to reservoirs involves additional simplifying assumptions, in terms of ignoring processes that are considered of secondary importance in regulating contaminant behavior in impoundments (Table 10). Also, the reservoir-specific screening methods consider a number of processes other than those listed in Table 10, which specifically determine contaminant transport and fate. These other processes include thermal stratification, sediment deposition and accumulation, nutrient-related eutroph'   _ion potential, and the coupled dynamics of dissolved oxygen and biochemical oxygen demand. A similar list of processes is included in the riverine-specific methods. These additional processes are important in that proper understanding of their role in influencing contaminant dynamics in the water body in question is essential to the assessment of potential contaminant problems.

305. One should recognize that these screening techniques yield predictions of maximum concentrations that could occur in reservoirs and other aquatic systems if steady-state conditions were ever achieved. However, since a variety of transient events always disrupt the attainment of truly steady-state behaviors, the predicted concentrations will almost always exceed field-measured values. Thus, these predictions essentially represent worst-case scenarios, with various levels of realism attached to them depending on the level of analysis at which a

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specific prediction was generated. The accurate prediction of contaminant concentrations would require the consideration of temporally and spatially variable kinetic processes at a level far too detailed to be useful as a screening tool for routine management application.

306. As emphasized earlier, these screening methods make numerous simplifying assumptions in order to provide a rapid assessment of contaminant problems in water bodies. They represent extremely useful and scientifically defensible management tools, but only if used with proper scientific and engineering judgment and with careful consideration of the likely errors contained in a given application. In particular, one should closely examine the likely sources of uncertainty in screening predictions of steady-state contaminant concentrations, by using ranges of values for kinetic coefficients rather than single point estimates.

Uses in managing reservoir contaminant problems

307. The primary goal of applying these screening methods to reservoirs is to identify the occurrence of specific contaminant problems in specific impoundments. However, the methods themselves are so general that they can be used for a variety of other related purposes, and at various times during the course of a reservoir monitoring program. In order to illustrate the types of uses which are possible, five specific examples of their use for interpreting monitoring data and evaluating reservoir management strategies will be discussed.

308. As mentioned in Part II, these screening methods can be useful in deciding whether a monitoring program is required at a specific CE project, as well as what specific variables from those listed in Tables 2 and 3 should be included. Together with estimates of contaminant loadings to a given reservoir and information from Mills et al. (1982) or other sources on contaminant properties and kinetic coefficients, the screening methods could be used to predict likely contaminant concentrations in the main pool of the impoundment. Existing data, perhaps derived from such sources as National Pollution Discharge Elimination System permit records or USGS gaging stations, could be used to estimate contaminant loadings. Alternatively, extensive information

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supplied in Mills et al. (1982) on contaminant loadings to aquatic environments, categorized by type of industrial and agricultural activity in the contributing watershed, would be useful in estimating the required data.

309. If, at any one of the three levels of analysis, the predicted concentration was less than the concentration specified in the applicable standard, one would conclude--with appropriate reservations based on the errors and simplifications inherent in the screening methods--that a water quality problem did not exist in that particular impoundment, and that field monitoring was not required. On the other hand, if the predicted concentration at each level of analysis exceeded the standard, then the need for some type of field monitoring effort would be indicated. This approach might be especially useful for reaching conclusions concerning the likelihood of contaminant problems in new or proposed reservoirs.

310. The screening methods could also be used to aid in interpreting specific results from a reservoir monitoring program, especially if measured concentrations exceeded relevant water quality standards. Here, screening predictions of contaminant concentrations would be compared with measured values in order to identify those processes which appear to be most important in regulating the environmental behavior of a given toxic chemical in the sampled reservoir. For example, if the contaminant concentration predicted from a first-level analysis was greater than the observed concentration, one would conclude that various speciation, transformation, and transport processes were important in regulating the dynamics of that contaminant.

311. By judiciously including or ignoring specific processes in second- and third-level analyses, one might be able to identify the combination of processes regulating contaminant dynamics in the sampled reservoir. Of course, appropriate scientific and engineering judgment would have to be employed in such an iterative application of the screening methods; one could not simply apply them in "cookbook" fashion. Through such an analysis, one might identify processes about which better information was required in order to understand the environmental

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behavior of the contaminant of interest. If so, then accessory intensive field studies of those specific processes might be warranted as part of a continuing monitoring program.

312. Knowledge of the specific processes that appear to be most important in regulating the behavior of specific contaminants in a given reservoir would be very useful in identifying management options which might be employed to reduce the severity of any contaminant problems observed. Thus, if the screening methods could be used successfully to identify key regulatory processes as suggested above, then they could also be used to identify and evaluate potentially useful management approaches. For example, if screening results demonstrated that sediment resuspension and subsequent desorption of contaminants into the water column were much more important in determining contaminant levels in a given reservoir than loadings from upstream sources, this would suggest the application of very different management techniques than if the converse were true.

313. The judicious application of screening methods could also provide a means of evaluating the success of the management options so identified. This would involve estimating the effects of the candidate management procedures on the key regulatory processes, and then predicting the changes in contaminant concentrations resulting from application of the several management options. Thus, the screening methods could be used not only to identify feasible management options, but also to evaluate their likelihood of success in reducing the magnitude of specific contaminant problems. Again, this represents an unusual application of screening procedures to the assessment of reservoir contaminant problems, and requires that careful attention be given to likely sources of error and uncertainty in the methods so as to avoid serious errors in judgment.

314. A fourth important use of the screening methods would be to identify specific instances in which a more refined analysis was required before any reliable decisions on reservoir management could be reached. For example, application of screening procedures to the results of a given monitoring program could fail to identify with any

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degree of certainty which processes were regulating the behavior of the
contaminants of interest, or could fail to yield any defensible conclu-
sions concerning useful management options. In such instances, the only
reasonable conclusion to reach would be that a more detailed analysis of
the problem was warranted, perhaps involving the select intensive field
studies combined with a detailed water quality modeling study using an
available numerical model. Deciding when more detailed approaches are
warranted represents a valid and cost-effective use of screening
methods. It simply is not possible to take in-depth approaches to all
possible reservoir contaminant problems; screening methods can be used
reliably to identify specific situations where more intensive analyses
are needed.

315. A final useful application of screening methods in relation
to managing reservoir contaminant problems involves deciding whether and
when the reevaluation of a specific reservoir may be required. For
example, data on existing water quality conditions in a given reservoir
could be used together with information on projected land-use changes in
the contributing watershed to decide whether substantial future changes
in reservoir contaminant concentrations are likely, and whether a future
monitoring program may be required. Given the persistence of toxic
chemicals in the environment, and the continued synthesis of new and
potentially toxic organic chemicals in this nation's industrial labora-
tories, the continuing evaluation of reservoirs for the presence of con-
taminant problems seems likely. The screening methods discussed here
represent particularly useful management tools for this purpose.

Other available approaches

316. Although the screening methods published by EPA (Mills
et al. 1982) and discussed in detail here represent the most comprehen-
sive set of management tools for evaluating contaminant problems in res-
ervoirs in relation to field monitoring programs, they are not the only
such tools available. In particular, these methods are quite similar to
an extensive body of approaches developed for predicting the eutrophica-
tion potential of lakes and reservoirs. These techniques were specifi-
cally developed for use with conventional pollutants, but could be

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adapted for use in relation to toxic pollutants. The following sources should be consulted for information on these approaches: EM 1110-2-1201, Reckhow and Chapra (1983), and Walker (1982).

317. One particularly useful feature of these methods for predicting eutrophication potential is the availability of statistical approaches for assessing sources and levels of uncertainty in predicted reservoir water quality conditions. These statistical approaches could be adapted for application to contaminant problems in reservoirs. Reckhow and Chapra (1983) provide a useful introduction to the extensive literature on proper procedures for examining model prediction uncertainty.

Management Options

318. The final step in a reservoir contaminant monitoring program involves identifying, evaluating, and implementing specific management approaches for reducing the severity of any problems discovered. All data management, analysis, and interpretation procedures employed as part of the monitoring program should be designed to facilitate this goal. However, successful realization of this goal may be difficult, for a variety of reasons cited in previous parts of this report.

a. Insufficient or inappropriate data can hinder the development of management conclusions.

b. The identification of management approaches useful for mitigating existing contaminant problems requires supporting information on contaminant sources, properties, and environmental behavior. Yet much of this information is currently of a preliminary nature, and much remains to be learned about contaminants in reservoirs.

c. Management of contaminant problems in multipurpose reservoirs may involve compromises among conflicting water quality objectives associated with different project purposes.

d. The potential impacts of toxic chemical contaminants on the health of human and aquatic populations using a given reservoir are more severe than are the impacts of more conventional water quality parameters, such as dissolved oxygen depletion or plant nutrients.

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<u>e</u>. The same general limited range of management options is available for managing contaminant problems as is currently available for other water quality concerns. Consequently, additional operational constraints are being placed on a limited number of management practices.

319. For all these reasons, the management of contaminant problems in reservoirs is difficult and costly and involves careful consideration of likely consequences of incorrect decisions. Although the detailed consideration of management approaches for reservoir contaminant problems is beyond the scope of this report, brief consideration is given below to the identification and evaluation of management options as part of the data interpretation phase. Other sources, such as Khalid et al. (1983), should be consulted for further details on management approaches currently being employed in CE reservoirs in dealing with contaminant problems.

320. Several key ideas must be kept in mind in identifying and evaluating management options for reservoir contaminant problems.

<u>a</u>. Partly because of the persistence of toxic chemicals in aquatic environments, it is not possible to eliminate contaminant problems. One can at most succeed in keeping them within acceptable bounds.

<u>b</u>. The pollution of reservoirs with toxic pollutants is a watershed-level problem; it is not a problem that can be confined to the specific reservoir in question. Thus, reservoir management is contingent upon management practices in effect in the contributing watershed. Moreover, management approaches employed in a given reservoir will impact a number of downstream aquatic systems as well. Clearly, then, the management of reservoirs in relation to the occurrence of contaminant problems is only one part of the management of contaminant problems in entire water resource systems or networks. Reservoir management cannot be isolated from this larger context, for contaminant or any other water quality problems.

<u>c</u>. In order to identify potentially successful management approaches for reducing the severity of any contaminant problems observed in a given reservoir, one must have a relatively good understanding of current contaminant concentrations in reservoirs, as well as knowledge of contaminant sources and understanding of the key processes regulating the environmental behavior of the contaminants in question. In the absence of such specific information, uncertainty will continue to plague

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reservoir management. As discussed in this report, the intent of monitoring programs is to supply exactly this information, and thereby to facilitate the proper management of reservoirs in relation to the possible occurrence of toxic chemicals in reservoir waters, sediments, and biota.

321. In considering possible reservoir management strategies for reducing the severity of any detected contaminant problems, a basic distinction must be made. That is, are significant loadings or inputs of contaminants from the contributing watershed still occurring? Different types of management concerns and possibilities must be considered in reservoirs impacted by continuing contaminant loadings than in those where contaminant loadings from external sources have been controlled.

322. If significant contaminant loadings to the reservoir in question are still occurring, the range of possible management approaches for mitigating observed water quality problems will be quite constrained. In such circumstances, the only viable management approach may involve either retaining the toxic chemicals within the impoundment or passing them downstream, preferably at diluted concentrations. Such management approaches could involve the use of multilevel withdrawal structures, with the intent being either to prevent contaminant losses in outflows altogether or to dilute contaminant concentrations to lower, acceptable levels. Alternatively, management might involve use of some type of trap to contain inputs of contaminated sediments, thus confining the majority of the problem to a small portion of the upper reaches of the reservoir. Clearly, all such approaches are temporary and "stop-gap"; in such circumstances, the overwhelming management concern is to control loadings from the surrounding watershed.

323. Management concerns and possibilities in reservoirs no longer being subjected to contaminant inputs are quite different from those described in the previous paragraph. For such impoundments, the major continuing problems are likely to be associated with releases of toxic chemicals from contaminated sediments at slow rates over long time periods. As continuing sedimentation buries contaminated sediments under newer, clean materials, existing problems may tend to diminish with time. In the interim, however, various management approaches

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should be employed to reduce the magnitude of current problems. For especially contaminated sediments, dredging may be a viable option for reducing contaminant inputs to the water column. If anaerobic conditions occur and lead to higher contaminant release rates, then approaches such as artificial destratification and hypolimnetic aeration should be considered in order to mitigate existing problems. Depending on the identity and properties of the contaminants being released from sediments, various chemical control methods might be applied to reduce inputs to the water column. Again, multilevel withdrawal structures would prove helpful in reducing contaminant loadings to downstream systems in reservoir outflow.

324. Whatever generic management approaches seem appropriate for reducing the magnitude of existing contaminant problems in a given reservoir, they must be adapted for use at that impoundment in a highly site-specific manner. Specific management strategies must be identified based on thorough analyses of available data on contaminant concentrations in reservoir waters, sediments, and biota. Such analyses should include rigorous statistical analyses and application of relevant screening procedures, as well as perhaps the use of numerical water quality models if suggested by other analyses.

325. Management options so identified should be carefully evaluated for their likelihood of success in reducing the severity of existing contaminant problems through the application of screening methods as well as more refined analyses such as numerical models. As with the design of monitoring programs, the management of reservoir contaminant problems must be adapted to the specific characteristics of the reservoir under study, and must be sufficiently flexible to allow modification over time as the nature of the existing contaminant problems changes. Well-designed and carefully conducted monitoring programs can contribute substantially to the sound management of potential contaminant problems in CE reservoirs, but only if the general guidelines provided in this report are carefully considered and followed.

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REFERENCES

American Chemical Society (ACS) Committee on Environmental Improvement, Subcommittee on Environmental Analytical Chemistry. 1980. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," _Analytical Chemistry_, Vol 52, pp 2242-2249.

American Public Health Association. 1981a. _Standard Methods for the Examination of Water and Wastewater_, 15th ed., Washington, DC.

_____. 1981b. _Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency_, Washington, DC.

American Society for Testing and Materials. 1982. _Annual Book of ASTM Standards, Part 31: Water_, Philadelphia, Pa.

Association of Official Analytical Chemists. 1980. _Official Methods of Analysis of the Association of Official Analytical Chemists_, 13th ed., Washington, DC.

Baker, R. A. 1980. _Contaminants and Sediments, Volume 2: Analysis, Chemistry, and Biology_, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.

Ballinger, D. G. 1979. "Effluent and Compliance Monitoring Programs Mandated by EPA," _Establishment of Water Quality Monitoring Programs_, American Water Resources Association, Minneapolis, Minn., pp 261-265.

Bicking, C. A., Olin, S., and King, P. 1978. "Procedure for the Evaluation of Environmental Monitoring Laboratories," EPA-600/4-78-017, US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Box, G. E. P., and Jenkins, G. M. 1976. _Time Series Analysis: Forecasting and Control_, Holden-Day, Inc., San Francisco, Calif.

Box, G. E. P., Hunter, W. G., and Hunter, J. S. 1978. _Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building_, John Wiley and Sons, Inc., New York.

Briggs, J. C. 1979. "Nationwide Surface Water Quality Monitoring Networks of the US Geological Survey," _Establishment of Water Quality Monitoring Programs_, American Water Resources Association, Minneapolis, Minn., pp 49-57.

Brown, E., Skougstad, M. W., and Fishman, M. J. 1970. "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and

Gases," Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter Al, US Geological Survey, Washington, DC.

Callahan, M. A., et al. 1979. "Water-Related Environmental Fate of 129 Priority Pollutants, Volumes I and II," prepared by Versar, Inc., Springfield, Va., for the US Environmental Protection Agency (available from NTIS, No. PB80-204373).

Casey, D., Nemetz, P. N., and Uyeno, D. H. 1983. "Sampling Frequency for Water Quality Monitoring: Measures of Effectiveness," Water Resources Research, Vol 19, pp 1107-1110.

Chatfield, E. J., et al. 1983. "Asbestos Fiber Determination in Water Samples: Preparation Techniques, Improved Analytical Method, and Rapid Screening," EPA-600/S4-83-044, prepared by the Ontario Research Foundation, Mississauga, Ontario, Canada, for the US Environmental Protection Agency, Environmental Research Laboratory, Athens, Ga.

Cochran, W. G. 1963. Sampling Techniques, John Wiley and Sons, Inc., New York.

Committee on Water Quality. 1977. Proceedings of a Seminar on Water Quality Data Collection and Management, US Army Corps of Engineers, Washington, DC.

_____. 1978. Proceedings of a Seminar on Water Quality Data Interpretation, US Army Corps of Engineers, Washington, DC.

_____. 1980. Proceedings of a Seminar on Water Quality Evaluation, US Army Corps of Engineers, Washington, DC.

_____. 1982. Proceedings of a Seminar on Attaining Water Quality Goals Through Water Management Procedures, US Army Corps of Engineers, Washington, DC.

_____. 1984. Proceedings of a Seminar on Applications in Water Quality Control, US Army Corps of Engineers, Washington, DC.

Drapier, N. R., and Smith, H. 1981. Applied Regression Analysis, 2d ed., John Wiley and Sons, Inc., New York.

Engler, R. M. 1981. "Contracting for Water Quality Data," Appendix A of "Guidelines for Contracting Biological and Chemical Evaluations of Dredged Material," P. Lang, et al., prepared by US Army Engineer Waterways Experiment Station, Vicksburg, Miss., for the US Army Engineer District, New York.

Erlebach, W. E. 1979. "A Systematic Approach to Monitoring Trends in the Quality of Surface Waters," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 7-19.

Federal Register. 1984 (24 Oct). "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," Vol 49, No. 209.

Fishman, M. J., and Brown, E. 1976. "Selected Methods of the U. S. Geological Survey for Analysis of Wastewaters," Open-file report 76-177, US Geological Survey, Washington, DC.

Ford, D. E., and Johnson, M. C. 1983. "An Assessment of Reservoir Density Currents and Inflow Processes," Technical Report E-83-7, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Friedman, L. C., and Erdmann, D. E. 1980. "Quality Assurance Practices," US Geological Survey, Denver Federal Center, Lakewood, Colo.

Gambrell, R. P., et al. 1984. "The Recovery of DDT, Kepone, and Permethrin Added to Soil and Sediment Suspensions Incubated Under Controlled Redox Potential and pH Conditions," Journal of the Water Pollution Control Federation, Vol 56, pp 174-182.

Gaugush, R. F., et al. 1984. "Statistical Methods for Reservoir Water Quality Investigations," Instruction Report in preparation, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Gaul, J. A., and McMahon, B. M., eds. 1983. "Pesticide Analytical Manual, Volumes I: Multiresidues and II: Individual Residues," US Food and Drug Administration, US Department of Health and Human Services, Rockville, Md.

Goerlitz, D. F., and Brown, E. 1972. "Methods for Analysis of Organic Substances in Water," Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A3, US Geological Survey, Washington, DC.

Green, R. H. 1979. Sampling Design and Statistical Methods for Environmental Biologists, John Wiley and Sons, Inc., New York.

Gunkel, R. C., Jr., et al. 1984. "A Comparative Study of Sediment Quality in Four Reservoirs," Technical Report E-84-2, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Keeley, J. W., et al. 1978. "Reservoirs and Waterways; Identification and Assessment of Environmental Quality Problems and Research Program Development," Technical Report E-78-1, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Khalid, R. A., et al. 1983. "Literature Survey of Reservoir Contaminant Problems," Technical Report E-83-13, prepared by Louisiana State University, Baton Rouge, La., for the US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Kratochvil, B., and Taylor, J. K. 1981. "Sampling for Chemical Analysis," Analytical Chemistry, Vol 53, pp 924A-938A.

Lang, P., et al. 1981. "Guidelines for Contracting Biological and Chemical Evaluations of Dredged Material," prepared by US Army Engineer Waterways Experiment Station, Vicksburg, Miss., for US Army Engineer District, New York.

Langford, R. H. 1979. "National Monitoring of Water Quality," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 1-6.

Lind, O. T. 1974. Handbook of Common Methods in Limnology, C. V. Mosby Company, St. Louis, Mo.

Loftis, J. C., and Ward, R. C. 1979. "Statistical Tradeoffs in Monitoring Network Design," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 36-48.

Loftis, J. C., Ward, R. C., and Smillie, G. M. 1983. "Statistical Models for Water Quality Regulation," Journal of the Water Pollution Control Federation, Vol 55, pp 1098-1104.

Longbottom, J. E., and Lichtenberg, J. J., eds. 1982. "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. 1982. Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds, McGraw-Hill Book Company, New York.

Mills, W. B., et al. 1982. "Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants, Parts I and II," EPA-600/6-82-004a, prepared by Tetra Tech, Inc., Lafayette, Calif., for the US Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Ga.

Morrison, D. F. 1976. Multivariate Statistical Methods, 2d ed., McGraw-Hill Book Company, New York.

Mosteller, F., and Tukey, J. W. 1977. Data Analysis and Regression: A Second Course in Statistics, Addison-Wesley Publishing Company, Inc., Reading, Mass.

Parzen, E. 1960. Modern Probability Theory and Its Applications, John Wiley and Sons, Inc., New York.

Plumb, R. H., Jr. 1981. "Procedures for Handling and Chemical Analysis of Sediment and Water Samples," Technical Report EPA/CE-81-1, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Reckhow, K. H. 1979a. "Quantitative Techniques for the Assessment of Lake Quality," EPA-440/5-79-015, prepared by Michigan State University, East Lansing, for the Environmental Protection Agency, Office of Water Planning and Standards, Washington, DC.

_____. 1979b. "Sampling Designs for Lake Phosphorus Budgets," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 285-306.

Reckhow, K. H., and Chapra, S. C. 1983. Engineering Approaches for Lake Management, Volume 1: Data Analysis and Empirical Modeling, Butterworth Publishers, Boston, Mass.

Rice, J. M., and Anderson, D. E. 1979. "Useful Monitoring for Policy and Decision Makers," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 363-369.

Sanders, T. G., and Ward, R. C. 1979. "Relating Stream Standards to Regulatory Water Quality Monitoring Practices," Establishment of Water Quality Monitoring Programs, American Water Resources Association, Minneapolis, Minn., pp 339-348.

Saul, G. E., et al. 1982. "Data-Base Management System for Reservoir Field Studies," EWQOS Information Exchange Bulletin, Vol E-82-1, pp 1-4.

Shapiro, J., and Swain, E. B. 1983. "Lessons from the Silica 'Decline' in Lake Michigan," Science, Vol 221, pp 457-459.

Sherma, J. 1976. "Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples," prepared by Lafayette College, Easton, Pa, for US Environmental Protection Agency, Office of Research and Development, Health Effects Research Laboratory, Research Triangle Park, N. C.

Siegel, S. 1956. Nonparametric Statistics for the Behavioral Sciences, McGraw-Hill Book Company, New York.

Slack, K. V., et al. 1973. "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples," Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A4, US Geological Survey, Washington, DC.

Snedecor, G. W., and Cochran, W. G. 1972. *Statistical Methods*, 7th ed., Iowa State University Press, Ames, Iowa.

Sokal, R. R., and Rohlf, F. ᵀ. 1979. *Biometry: The Principles and Practice of Statistics in Biological Research*, 2d ed., W. H. Freeman and Company, San Francisco, Calif.

Steel, R. G. D., and Torrie, J. H. 1980. *Principles and Procedures in Statistics*, 2d ed., McGraw-Hill Book Company, New York.

Stratton, C. L., and Bonds, J. D. 1979. "Quality Assurance Guidelines for ᴵERL-CI Project Officers," EPA-600/9-79-046, US Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

Stumm, W., and Morgan, J. J. 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2d ed., John Wiley and Sons, Inc., New York.

Thornton, K. W., et al. 1981. "Reservoir Sedimentation and Water Quality - An Heuristic Model," *Proceedings of a Symposium on Surface Water Impoundments*, American Society of Civil Engineers, Minneapolis, Minn., Vol I, pp 654-661.

_____. 1982. "Reservoir Water Quality Sampling Design," *Water Resources Bulletin*, Vol 18, pp 471-480 (reissued by OCE as EC 1110-2-233).

Tinsley, I. J. 1979. *Chemical Concepts in Pollutant Behavior*, John Wiley and Sons, Inc., New York.

Tukey, J. W. 1977. *Exploratory Data Analysis*, Addison-Wesley Publishing Company, Inc., Reading, Mass.

US Environmental Protection Agency. 1976. *Quality Criteria for Water*, Washington, DC.

_____. 1978. "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater" (Interim, Pending Issuance of Methods for Organic Analysis of Water and Wastes), Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

_____. 1979a. "Ambient Water Quality Criteria, 65 Pollutants," Criteria and Standards Division, Office of Water Planning and Standards, Washington, DC.

_____. 1979b. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

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US Environmental Protection Agency. 1979c. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

_____. 1980. "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples," EPA-600/8-80-038, Environmental Toxicology Division, Health Effects Research Laboratory, Research Triangle Park, N. C.

_____. 1982. "Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA-600/4-82-029, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

US Food and Drug Administration. 1979. Administrative Guidelines Manual, Washington, DC.

US Geological Survey. 1977. "National Handbook of Recommended Methods for Water-Data Acquisition," prepared under the sponsorship of the Office of Water Data Coordination, US Department of the Interior, Reston, Va.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals, 2d ed., Van Nostrand-Reinhold Company, New York.

Walker, W. W., Jr. 1981. "Empirical Methods for Predicting Eutrophication in Impoundments; Report 1, Phase I: Data Base Development," Technical Report E-81-9, prepared for the US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Walker, W. W., Jr. 1982. "Empirical Methods for Predicting Eutrophication in Impoundments; Report 2, Phase II: Model Testing," Technical Report E-81-9, prepared for the US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

_____. 1984. "Empirical Methods for Predicting Eutrophication in Impoundments; Report 3, Phase II: Model Requirements," Technical Report E-81-9, prepared for the US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Weber, C. I., ed. 1973. "Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents," EPA-670/4-73-001, US Environmental Research Center, Cincinnati, Ohio.

Welch, P. S. 1948. Limnological Methods, Blakiston Co., Philadelphia, Pa.

Wetzel, R. G., and Likens, G. E. 1979. Limnological Analyses, W. B. Saunders Company, Philadelphia, Pa.

Wolman, M. G. 1971. "The Nation's Rivers," _Science,_ Vol 174, pp 905-918.

Zison, S. W., Haven, K., and Mills, W. B. 1977. "Water Quality Assessment: A Screening Methodology for Nondesignated 208 Areas," EPA-600/9-77-023, prepared by Tetra Tech, Inc., Lafayette, Calif., for the US Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Ga.

Table 1

Summary of Select Properties of Conventional and Toxic Pollutants*

Property	Conventional	Toxic
Number of pollutants in category	10-25	100-1000; more being synthesized
Mode of origin	Typically natural	Mostly synthetic
Quantity of pollutant required to produce adverse impact	Typically large (e.g., 1000 kg/day)	Can be small (e.g., few kilograms/day)
Typical concentration range	ppm (mg/ℓ, mg/kg)	ppb (μg/ℓ, μg/kg) or lower
Major form for environmental transport	Dissolved or adsorbed to sediments	Typically highly adsorbed to sediments
Mean residence time in reservoir	Approximately equal to water residence time	Often much greater than water residence time
Capability for biodegradation	Natural or may biodegrade to harmless substance	May be transformed into compound of equal or greater toxicity; may resist biodegradation but bioconcentrate

* Modified from Mills et al. (1982).

Table 2

List of Chemical Contaminants Covered by Relevant
Water Quality Criteria and Standards*

Chemical Contaminant	Relevant Criteria**
Acenaphthene	EPA76, EPA80
Acrolein	EPA76, EPA80
Acrylonitrile	EPA76, EPA80
Aldrin, dieldrin	EPA76, EPA80, FDA, S
Antimony	EPA76, EPA80
Arsenic	EPA76, EPA80, PHS, S
Asbestos	EPA76, EPA80
Benzene	EPA76, EPA80
Benzidine	EPA76, EPA80
Beryllium	EPA76, EPA80
Cadmium	EPA76, EPA80, PHS, S
Carbon tetrachloride	PA76, EPA80
Chlordane	EPA76, EPA80, FDA, S
Chlorinated benzenes	EPA76, EPA80
Chlorinated ethanes	EPA76, EPA80
Chloroalkyl ethers	EPA76, EPA80
Chlorinated naphthalene	EPA76, EPA80
Chlorinated phenols	EPA76, EPA80
Chloroform	EPA76, EPA80

(Continued)

* Based on information tabulated in Khalid et al. (1983). The
  so-called "List of 65" pollutants are listed first, followed by other
  chemicals covered by relevant criteria.
** Symbols refer to relevant water quality criteria summarized in
  Part I. EPA76 and EPA80 refer to the 1976 EPA Red Book and the 1980
  EPA criteria, respectively. FDA refers to the FDA guidelines on
  toxicant concentrations in edible freshwater species; PHS, to the PHS
  National Drinking Water Standards; and S, to various State water
  quality standards.

(Sheet 1 of 3)

Table 2 (Continued)

Chemical Contaminant	Relevant Criteria**
2-chlorophenol	EPA76, EPA80
Chromium	EPA76, EPA80, PHS, S
Copper	EPA76, EPA80, PHS, S
Cyanides	EPA76, EPA80
DDT	EPA76, EPA80, FDA, S
Dichlorobenzenes	EPA76, EPA80
Dichlorobenzidine	EPA76, EPA80
Dichloroethylenes	EPA76, EPA80
2-4-dichlorophenol	EPA76, EPA80
Dichloropropanes/propenes	EPA76, EPA80
2,4-dimethylphenol	EPA76, EPA80
Dinitrotoluene	EPA76, EPA80
Diphenylhydrazine	EPA76, EPA80
Endosulfan	EPA76, EPA80
Endrin	EPA76, EPA80, FDA, PHS, S
Ethylbenzene	EPA76, EPA80
Fluoranthene	EPA76, EPA80
Haloethers	EPA76, EPA80
Halomethanes	EPA76, EPA80
Heptachlor	EPA76, EPA80, FDA, S
Hexachlorobutadiene	EPA76, EPA80
Hexachlorocyclohexane	EPA76, EPA80, PHS, S
Hexachlorocyclopentadiene	EPA76, EPA80
Isophorone	EPA76, EPA80
Lead	EPA76, EPA80, PHS, S
Mercury	EPA76, EPA80, FDA, PHS, S
Naphthalene	EPA76, EPA80
Nickel	EPA76, EPA80, S

(Continued)

(Sheet 2 of 3)

Table 2 (Concluded)

Chemical Contaminant	Relevant Criteria*
Nitrobenzene	EPA76, EPA80
Nitrophenols	EPA76, EPA80
Nitrosamines	EPA76, EPA80
Pentachlorophenol	EPA76, EPA80
Phenol	EPA76, EPA80
Phthalate esters	EPA76, EPA80
Polychlorinated biphenyls (PCBs)	EPA76, EPA80, FDA, S
Polynuclear aromatic hydrocarbons	EPA76, EPA80
Selenium	EPA76, EPA80, PHS, S
Silver	EPA76, EPA80, PHS, S
2,3,7,8-tetrachlorodibenzo-p-dioxin	EPA76, EPA80
Tetrachloroethylene	EPA76, EPA80
Thallium	EPA76, EPA80
Toluene	EPA76, EPA80
Toxaphene	EPA76, EPA80, FDA, S
Trichlorethylene	EPA76, EPA80
Vinyl chloride	EPA76, EPA80
Zinc	EPA76, EPA80, PHS, S
Iron	EPA76, PHS, S
Manganese	EPA76, PHS, S
pH	EPA76, PHS, S
Diazinon	S
Guthion	EPA76, S
Kepone	FDA
Malathion	EPA76, S
Methoxychlor	EPA76, PHS, S
Mirex	EPA76, FDA
Parathion	EPA76, S
2,4-D	EPA76, PHS, S
2,4,5-TP (Silvex)	EPA76, PHS, S

(Sheet 3 of 3)

Table 3
List of 129 Priority Pollutants*

I. Purgeable Organics

A. Purgeables:

Benzene (a, b)**	Chloroform (a, b)
Chlorobenzene (a)	1,1-dichloroethylene (a)
Toluene (a, b)	1,2-trans-dichloroethylene (a)
Ethylbenzene (a, b)	1,2-dichloropropane (a)
Carbon tetrachloride (a)	1,3-dichloropropene (a)
1,1-dichloroethane (a)	Methylbromide (a)
1,2-dichloroethane (a)	Methylchloride (a)
1,1,1-trichloroethane (a)	Methylenechloride (a, b)
1,1,2-trichloroethane (a)	Bromoform (a)
1,1,2,2-tetrachloroethane (a)	Dichlorobromomethane (a)
Chloroethane (a)	Trichlorofluoromethane (a)
Chlorodibromomethane (a)	Dichlorodifluoromethane (a)
Tetrachloroethylene (a)	Trichloroethylene (a)
Vinyl chloride	

B. Acrolein and acrylonitrile:

Acrolein (a)	Acrylonitrile (a)

II. Base/Neutral Extractable Organics

A. Phthalate esters:

Dimethyl phthalate	Di-n-octyl phthalate
Diethyl phthalate	Bis(2-ethylhexyl) phthalate (b)
Di-n-butyl phthalate (b)	Butylbenzyl phthalate

(Continued)

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* Modified from listings in US EPA (1982) and Mills et al. (1982).
  Each pollutant shown in this table is also listed in Table 2 either
  individually or generically.
** Small letters in parentheses following pollutant name have the
  following meaning:
  a = cited as volatile organic by Mills et al. (1982).
  b = cited by Mills et al. (1982) as a pollutant frequently discharged
      into the Nation's waterways.

Table 3 (Continued)

B. Haloethers:

Bis(2-chloroethyl) ether (a)	Bis(2-chloroethoxy) methane
Bis(2-chloroisopropyl) ether (a)	4-chlorophenylphenyl ether
2-chloroethyl vinyl ether (a)	4-bromophenylphenyl ether

C. Chlorinated hydrocarbons:

Hexachloroethane	1,3-dichlorobenzene (a)
Hexachlorobutadiene (a)	1,4-dichlorobenzene (a)
Hexachlorocyclopentadiene (a)	1,2,4-trichlorobenzene (a)
1,2-dichlorobenzene (a)	Hexachlorobenzene
2-chloronaphthalene	

D. Nitroaromatics and isophorone:

Nitrobenzene	2,4-dinitrotoluene
2,6-dinitrotoluene	Isophorone

E. Nitrosamines:

N-nitrosodimethylamine	N-nitrosodipropylamine
N-nitrosodiphenylamine	

F. Benzidines and hydrazines:

Benzidine	3,3'-dichlorobenzidine
1,2-diphenylhydrazine	

G. Polynuclear aromatic hydrocarbons:

Acenaphthene	Acenaphthylene
Fluoranthene (a)	Anthracene (a, b)
Naphthalene (b)	Benzo(g,h,i)perylene
Benzo(a)anthracene (a)	Fluorene
Benzo(a)pyrene (a)	Phenanthrene (a, b)
Benzo(b)fluoranthene	Dibenzo(a,h)anthracene
Benzo(k)fluoranthene	Indeno(1,2,3-c,d)pyrene
Chrysene	Pyrene

III. Acid Extractable Organics (Phenols)

Phenol (a, b)	Pentachlorophenol
2,4-dimethylphenol	4-chloro-3-methylphenol
2-chlorophenol	2-nitrophenol

(Continued)

Table 3 (Concluded)

2,4-dichlorophenol	4-nitrophenol
2,4 6-trichlorophenol	2,4-dinitrophenol
4,6-dinitro-2-methylphenol	

IV. Pesticides, PCB's, and Dioxin

A. Pesticides:

Aldrin (a)	Endrin
Dieldrin (a)	Endrin aldehyde
Chlordane (a)	Heptachlor (a)
4,4'-DDE (a)	Heptachlor epoxide
4,4'-DDD (a)	α – BHC
4,4'-DDT (a)	β – BHC
α – Endosulfan (a)	δ – BHC
β – Endosulfan (a)	γ – BHC
Endosulfan sulfate (a)	Toxaphene (a)

B. PCBs

Arochlor 1016 (a)	Arochlor 1248 (a)
Arochlor 1221 (a)	Arochlor 1254 (a)
Arochlor 1232 (a)	Arochlor 1260 (a)
Arochlor 1242 (a)	

C. Dioxin

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

V. Metals

Antimony	Mercury
Arsenic	Nickel (b)
Beryllium	Selenium
Cadmium	Silver
Chromium (b)	Thallium
Copper (b)	Zinc (b)
Lead (b)	

VI. Miscellaneous

Total cyanides (b)	Asbestos (fibrous)

Table 4

Summary of Statistical Formulae Relevant to the Determination of Sample Numbers, Allocation, and Frequency in Reservoir Contaminant Monitoring Programs*

Sampling Factor Being Determined	Equation		Definition of Symbols**

1. Simple Random Sampling

Total sample size

$$n = \frac{t^2 s^2}{d^2} \qquad (1)$$

- n = sample size
- t = tabulated value of Student's t distribution at specified level of significance
- s = sample variance
- d = specified level of precision in sample mean

Total sampling cost

$$C(n) = C_o + C_1 n \qquad (2)$$

- $C(n)$ = total cost for n samples
- C_o = fixed sampling cost
- C_1 = cost per individual sample

2. Stratified Random Sampling

Total sampling cost

$$C(n) = C_o + \sum_{i=1}^{k} C_1 n_1 \qquad (3)$$

- C_1 = cost per sample in i^{th} stratum
- k = number of discrete sampling strata
- n_i = sample size in i^{th} stratum, $\sum_{i=1}^{k} n_i = n$

(Continued)

* Summarized from information contained in Cochran (1963), Gaugush et al. (1984), Reckhow (1979a, 1979b), Reckhow and Chapra (1983), Thornton et al. (1982), and US EPA (1982).

** A given symbol is defined only once; it is not redefined on each subsequent use.

(Sheet 1 of 3)

Table 4 (Continued)

Sampling Factor Being Determined	Equation	Definition of Symbols
		s_i = sample standard deviation with i^{th} stratum

a. Equal Allocation

Total sample size

$$n = \frac{t^2\left(\sum_{i=1}^{k} s_i\right)^2}{d^2} \tag{4}$$

Sample size, i^{th} stratum

$$n_i = n/k \tag{5}$$

w_i = weighting factor for sampling within i^{th} stratum,

$$\sum_{i=1}^{k} w_i = 1$$

b. Proportional Allocation

Total sample size

$$n = \frac{t^2\left(\sum_{i=1}^{k} w_i s_i\right)^2}{d^2} \tag{6}$$

Sample size, i^{th} stratum

$$n_i = \frac{w_i s_i}{\sum_{i=1}^{k} w_i s_i}\, n \tag{7}$$

c. Optimal Allocation

Total sample size, fixed precision

$$n = \frac{t^2\left(\sum_{i=1}^{k} w_i s_i \sqrt{c_i}\right)\sum_{i=1}^{k}\left(w_i s_i/\sqrt{c_i}\right)}{d^2} \tag{8}$$

(Continued)

Table 4 (Concluded)

Sampling Factor Being Determined	Equation	Definition of Symbols**
Total sample size, fixed cost	$$n = \frac{[C(n) - c_0] \sum_{i=1}^{k} (w_i s_i/\sqrt{c_i})}{\left(\sum_{i=1}^{k} w_i s_i \sqrt{c_i}\right)} \quad (9)$$	
Sample size, i^{th} stratum	$$n_i = \frac{w_i s_i/\sqrt{c_i}}{\sum_{i=1}^{k} (w_i s_i/\sqrt{c_i})}\, n \quad (10)$$	

Table 5

Summary of Recommendations for Sample Volumes, Containers, Preservation, and Holding

Times for Analyses of Contaminant Concentrations in Environmental Samples*

Chemical Contaminant or Contaminant Class[1]	Sample Volume[2] (ml, ℓ)	Container[3]	Preservative[4,5]	Holding Time[6]	References[7]
Purgeable halocarbons[8]	25 ml[9]	G, Teflon-lined septum	Cool, 4° C 0.008% $Na_2S_2O_3$[10]	14 days	c, d, e
Purgeable aromatics[8]	25 ml[9]	G, Teflon-lined septum	HCl to pH ~2[11] Cool, 4° C 0.008% $Na_2S_2O_3$[10]	14 days	c, d, e
Acrolein and acrylonitrile	500 ml[9]	G, Teflon-lined septum	Adjust pH to 4-5 with acid or base[11] Cool, 4° C 0.008% $Na_2S_2O_3$[10]	14 days	c, d, e
Phenols – total			H_2SO_4 to pH <2 Cool, 4° C	28 days	a, b, c, d, e, f

(Continued)

* Explanations of footnotes 1-28 are provided at the conclusion of this table.

(Sheet 1 of 10)

Table 5 (Continued)

Chemical Contaminant or Contaminant Class[1]	Sample Volume[2] (ml, ℓ)	Container[3]	Preservative[4,5]	Holding Time[6]	References[7]
Phenols[12]	500 ml[13]	G, Teflon-lined cap	Cool, 4° C 0.008% $Na_2S_2O_3$[10]	7 days until extraction 40 days until analysis[14]	a, c, d, e
Benzidines[15]	500 ml[13]	G, Teflon-lined cap	Cool, 4° C, in dark[16] 0.008% $Na_2S_2O_3$[10] H_2SO_4 to pH 2-7[17]	7 days until extraction, 7 days until analysis[14,18]	c, d, e
Phthalate esters	500 ml[13]	G, Teflon-lined cap	Cool, 4° C	7 days until extraction. 40 days until analysis[14]	c, d, e
Nitrosamines	500 ml[13]	G, Teflon-lined cap	Cool, 4° C, in dark[16] 0.008% $Na_2S_2O_3$[10] Adjust pH to 7-10 with NaOH or H_2SO_4[19]	7 days until extraction, 40 days until analysis[14]	c, d, e

(Continued)

(Sheet 2 of 10)

Table 5 (Continued).

Chemical Contaminant or Contaminant Class[1]	Sample Volume[2] (ml, ℓ)	Container[3]	Preservative[4,5]	Holding Time[6]	References[7]
Organochlorine pesticides and PCB's	1 ℓ[13]	G, Teflon-lined cap	Cool, 4° C Adjust pH to 5-9 with NaOH or H_2SO_4[20] 0.008% $Na_2S_2O_3$[10,21]	7 days until extraction, 40 days until analysis[14]	a, c, d, e, f
Nitroaromatics and isophorone	500 ml	G, Teflon-lined cap	Cool, 4° C 0.008% $Na_2S_2O_3$[10]	7 days until extraction, 40 days until analysis[14]	c, d, e
Polynuclear aromatic hydrocarbons	500 ml[13]	G, Teflon-lined cap	Cool, 4° C, in dark[16] 0.008% $Na_2S_2O_3$[10]	7 days until extraction, 40 days until analysis[14]	c, d, e, f
Haloethers	500 ml[13]	G, Teflon-lined cap	Cool, 4° C 0.008% $Na_2S_2O_3$[10]	7 days until extraction, 40 days until analysis[14]	c, d, e

(Continued)

(Sheet 3 of 10)

Table 5 (Continued)

Chemical Contaminant or Contaminant Class [1]	Sample Volume [2] (ml, ℓ)	Container [3]	Preservative [4,5]	Holding Time [6]	References [7]
Chlorinated hydrocarbons	500 ml [13]	G, Teflon-lined cap	Cool, 4° C	7 days until extraction, 40 days until analysis [14]	c, d, e
Dioxin (TCDD) [22]	500 ml [13]	G, Teflon-lined cap	Cool, 4° C, in dark [16] 0.008% $Na_2S_2O_3$ [10]	7 days until extraction, 40 days until analysis [14]	c, d, e
Metals					
Chromium (hexavalent)	100 ml	P, G	Cool, 4° C	24 hr	c, d, f
Mercury	500 ml	G	HNO_3 to pH <2	28 days	b, c, d, f
All others	100 ml	P, G	HNO_3 to pH <2	6 months	a, b, c, d, f

(Continued)

(Sheet 4 of 10)

Table 5 (Continued)

Chemical Contaminant or Contaminant Class[1]	Sample Volume[2] (ml, l)	Container[3]	Preservative[4,5]	Holding Time[6]	References[7]
Miscellaneous					
Total cyanides	500 ml	P, G	Cool, 4° C NaOH to pH >12 0.6g ascorbic acid	14 days[23]	a, b, c, d
Asbestos (fibrous)[24]	—	—	—	—	—
Other Contaminants					
Metals[25]	100 ml	P, G	HNO_3 to pH <2	6 months	a, b, c, d, f
Hydrogen ion (pH)	30 ml	P, G	Determine onsite	2–6 hr	a, b, c, d, f
Organophosphorus pesticides[26]	1l	G, Teflon-lined cap	Cool, 4° C H_2SO_4 to pH <3 10 g Na_2SO_4	7 days until extraction, 40 days until analysis[14]	d, f

(Continued)

(Sheet 5 of 10)

Table 5 (Continued)

Chemical Contaminant or Contaminant Class[1]	Sample Volume[2] (ml, ℓ)	Container[3]	Preservative[4,5]	Holding Time[6]	References[7]
Organochlorine pesticides[27]	1ℓ	G, Teflon-lined cap	Cool, 4° C Adjust pH to 5-9 with NaOH or H_2SO_4[20]	7 days until extraction, 40 days until analysis[14]	d, f
Kepone[24]	---	---	---	---	---
Chlorinated phenoxy acid herbicides[28]	1ℓ	G, Teflon-lined cap	Cool, 4° C H_2SO_4 to pH <2	7 days until extraction 40 days until analysis	d, f

1 Refer to Table 3 for a listing of the individual chemical contaminants associated with each of the contaminant classes shown in this table. Compounds listed under "Other Contaminants" in this table are those listed at the end of Table 2 (i.e., following zinc), which are not included in the 1980 EPA criteria (i.e., the List of 65) or in the expanded list of priority pollutants (Table 3).

2 Volumes shown are the minimum volumes required for the specified analysis. So long as one is careful to check compatibilities among sample containers and preservation techniques, it may be possible to collect larger volumes in the field and then split into appropriate subsamples for analyses. In collecting samples, bottles should be filled completely when any constituent to be

(Continued)

(Sheet 6 of 10)

Table 5 (Continued)

analyzed will be adversely affected by the presence of air. This includes purgeable halocarbons and aromatics, acrolein and acrylonitrile, phenols, benzidines, nitrosamines, polynuclear aromatic hydrocarbons, haloethers, and pH. Sample containers for contaminants other than these need not be filled completely.

3 Preferred container types are either linear polyethylene (P) or borosilicate glass (G). For metal analyses, polyethylene containers having polypropylene caps (no liners) are preferred to glass.

4 Whenever possible, samples should be preserved in the field immediately after collection. The preservative should have been added to sample containers prior to their transport to the field to ensure that all portions of the sample are properly preserved without degradation. Sample should be shaken to mix the preservative uniformly. If it is not possible to preserve each sample at the time of collection, samples may be maintained at 4° C until the preservative can be added. The delay in preservation should be kept as short as possible.

5 When any sample is to be shipped by common carrier or sent through the US Mails, it must comply with the US Department of Transportation Hazardous Materials Regulations (49 C.F.R., Part 172) (US EPA 1982). The person shipping samples is responsible for ensuring compliance. The Office of Hazardous Materials, Materials Transportation Bureau, US Department of Transportation, has determined that these regulations do not apply to the following materials used in sample preservation: HCl in water solutions at concentrations of 0.04% by weight or less (pH ~1.96 or greater); HNO₃ in water solutions at concentrations of 0.15% by weight or less (pH ~1.62 or greater); H₂SO₄ in water solutions at concentrations of 0.35% by weight or less (pH ~1.15 or greater); and NaOH in water solutions at concentrations of 0.080% by weight or less (pH ~12.30 or less).

6 Samples should always be analyzed as soon as possible after collection. The holding times listed are the maximum times that samples may be held prior to analysis and still considered valid. These holding times assume that the specified preservation technique has been properly employed. Samples may be held for longer periods only if the analytical laboratory has data on

(Sheet 7 of 10)

(Continued)

Table 5 (Continued)

file to show that the specific types of samples are stable for longer periods. Conversely, the analytical laboratory is obligated to hold samples for shorter time periods if data exist to show that this is necessary to maintain sample stability for certain types of environmental samples.

7 References used in preparing this table are as follows: a - APHA 1981a; b - US EPA 1979b; c - US EPA 1982; d - Federal Register (1984), Vol 49; e - Longbottom and Lichtenberg 1982; f - Plumb 1981.

8 The purgeables listed in Table 3 were split into two groups to correspond with the EPA 600 Series Methods. Purgeable aromatics include benzene, chlorobenzene, toluene, and ethylbenzene. Purgeable halocarbons include all other contaminants listed under class I.A. purgeables in Table 3.

9 Sample containers should be filled in such a manner that no air bubbles pass through the sample. Containers should be sealed so that no air bubbles are trapped within.

10 Should be added only in the presence of residual chlorine.

11 For samples to be analyzed for acrolein, the holding time is reduced to 3 days in the absence of pH adjustment. For purgeable aromatics, the holding time is reduced to 7 days without pH adjustment.

12 Recommendations contained in the newer EPA methods for phenols (US EPA 1982, Longbottom and Lichtenberg 1982) differ from older recommendations, which include addition of H_3PO_4 to pH <4, addition of 1 g/ℓ $CuSO_4 \cdot 5H_2O$, and 24-hr holding time. The newer recommendations shown in this table should be followed.

13 Conventional sampling practices (e.g., ASTM 1982, Part 31, D3370) should be followed, except that the sample container should not be prerinsed or prewashed with the sample prior to collection.

(Continued)

Table 5 (Continued)

14 Times shown refer to number of days from sample collection until extraction, and number of days from sample extraction until analysis.

15 These recommendations apply only to benzidines, not to 1,2-diphenylhydrazine. The EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, may be contacted for recommendations for this latter contaminant.

16 The indicated contaminants are sensitive to light, and thus susceptible to photolytic degradation. Sample containers should be kept in the dark, or sample should be placed in amber or foil-covered containers.

17 If 1,2-diphenylhydrazine is likely to be present, pH should be adjusted to 4.0 ± 0.2 to prevent rearrangement to benzidine.

18 Extracts may be held for the indicated time only if stored under an inert (oxidant free) atmosphere and protected from light.

19 Required only for the analysis of diphenylnitrosamine.

20 pH adjustment may be omitted if samples are to be extracted within 72 hr.

21 Required only for the analysis of aldrin.

22 Sample containers containing dioxin (TCDD) or extracts should be clearly labeled POISON.

23 Holding time reduced to 24 hr if sulfide present.

24 Contact the EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, for recommendations for this contaminant.

25 Includes iron and manganese from Table 2.

(Continued)

Table 5 (Concluded)

26 Includes diazinon, guthion, malathion, and parathion from Table 2.

27 Includes methoxychlor and Mirex from Table 2.

28 Includes 2,4-D; 2,4,5-TP (Silvex) from Table 2.

Table 6

Summary of Approved and Recommended Analytical Methods for Determining Contaminant Concentrations in Environmental Samples*

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Purgeable halocarbons[8]						
Carbon tetrachloride	GC / GC/MS	601 / 624,1624	S102 / –	– / –	– / –	b,130 / –
Chloroform	GC / GC/MS	601 / 624,1634	S92,S102 / –	D3973 (732) / –	– / –	b,130 / –
Bromoform	GC / GC/MS	601 / 624,1624	S92 / –	D3973 (732) / –	– / –	– / –
1,1,1-trichloroethane	GC / GC/MS	601 / 624,1624	– / –	?3973 (732) / –	– / –	– / –
1,1,2-trichloroethane	GC / GC/MS	601 / 624,1624	S102 / –	– / –	– / –	b,130 / –
1,1,2,2-tetrachloroethane	GC / GC/MS	601 / 624,1624	S102 / –	– / –	– / –	b,136 / –
Trichloroethylene	GC / GC/MS	601 / 624,1624	S92 / –	– / –	– / –	– / –
Tetrachloroethylene	GC / GC/MS	601 / 624,1624	S102 / –	D3973 (732) / –	– / –	b,130 / –
Chlorodibromomethane	GC / GC/MS	601 / 624,1624	S92 / –	D3973 (732) / –	– / –	– / –

(Continued)

* Explanations of footnotes 1-18 are provided at the conclusion of this table.

(Sheet 1 of 12)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class [1]	Method [2]	EPA Methods [3]	Standard Methods 15th Ed. [4]	ASTM Methods [5]	USGS Methods [6]	Other Approved Methods [7]
Purgeable halocarbons (Cont.)						
Dichlorobromomethane	GC	601	S92	D3973 (732)	--	--
	GC/MS	624,1624	--	--	--	--
Methylene chloride	GC	601	S102	--	--	b,130
	GC/MS	624,1624	--	--	--	--
All others [9]	GC	601	--	--	--	--
	GC/MS	624,1624	--	--	--	--
Purgeable aromatics [8]						
Chlorobenzene	GC	601,602	S102	--	--	b,130
	GC/MS	624,1624	--	--	--	--
All others [9]	GC	602	--	--	--	--
	GC/MS	624,1624	--	--	--	--
Acrolein and acrylonitrile						
Acrolein	GC	603	--	--	--	--
	GC/MS	624[10],1624	--	--	--	--
Acrylonitrile	GC	603	--	D2908,D3374 (660,749)	--	d,5-126
	GC/MS	624[10],1624	--	--	--	--
Phenols						
Pentachlorophenol	GC	604	S50	--	--	b,140;d,5-126
	GC/MS	625,1625	--	--	--	--
All others [9]	GC	604	--	D1783 (789)	--	--
	GC/MS	625,1625	--	--	--	--

(Continued)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Benzidines and hydrazines						
Benzidine	GC	605	248	-	-	b,1;d,5-125
	GC/MS	625[11],1625	-	-	-	-
	HPLC	605	-	-	-	-
3,3'-dichlorobenzidine	GC	605	-	-	-	-
	GC/MS	625,1625	-	-	-	-
	HPLC	605	-	-	-	-
1,2-diphenylhydrazine[12]	-	-	-	-	-	-
Phthalate esters	GC	606	-	-	-	-
	GC/MS	625,1625	-	-	-	-
Nitrosamines	GC	607	-	-	-	-
	GC/MS	625[11],1625	-	-	-	-
Organochlorine pesticides						
Aldrin	GC	608	509A,873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
α-BHC	GC	608	509A (493)	D3086 (765)	-	b,7;f,10A-1
	GC/MS	625[11]	-	-	-	-
β-BHC	GC	608	-	D3086 (765)	-	f,10A-1
	GC/MS	625	-	-	-	-
δ-BHC	GC	608	-	D3086 (765)	-	-
	GC/MS	625	-	-	-	-
γ-BHC (Lindane)	GC	608	509A,873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625[11]	-	-	-	-

(Continued)

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Table 6 (Continued)

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Organochlorine pesticides (Cont.)						
Chlordane	GC	608	509A (493)	D3086 (765)	-	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
4,4'-DDD	GC	608	509A[13],873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
4,4'-DDE	GC	608	509A,873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
4,4'-DDT	GC	608	509A,873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
Dieldrin	GC	608	509A[13],873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
α-Endosulfan	GC	608	509A (493)	D3086 (765)	-	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
β-Endosulfan	GC	608	509A (493)	D3086 (765)	-	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625[11]	-	-	-	-
Endosulfan sulfate	GC / GC/MS	608 625	-	-	-	-
Endrin	GC	608	509A,873 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625[11]	-	-	-	-
Endrin aldehyde	GC / GC/MS	608 625	-	-	-	-

(Continued)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Organochlorine pesticides (Cont.)						
Heptachlor	GC	608	509A,573 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
Heptachlor epoxide	GC	608	509A,573 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
	GC/MS	625	-	-	-	-
Toxaphene	GC	608	509A,573 (493)	D3086 (765)	30	b,7;d,5-131;f,10A-1
	GC/MS	625	-	-	-	-
PCB's						
Arochlor 1248,1254,1260	GC	608	878	D3534 (804)	-	b,43;c,3-289;d,5-138; f,10A-1
	GC/MS	625	-	-	-	-
Arochlor 1016,1221,1232,1242	GC	608	878	D3534 (804)	-	b,43;d,5-138
	GC/MS	625	-	-	-	-
Nitroaromatics and isophorone	GC	609	-	-	-	-
	GC/MS	625,1625	-	-	-	-
Polynuclear aromatic hydrocarbons	GC	610	-	-	-	-
	GC/MS	625,1625	-	-	-	c,3-337
	HPLC	610	-	-	-	-
Haloethers						
2-chloroethyl vinyl ether	GC	601	-	-	-	-
	GC/MS	624,1624	-	-	-	-
All others[9]	GC	611	-	-	-	-
	GC/MS	625,1625	-	-	-	-

(Continued)

(Sheet 5 of 12)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class [1]	Method [2]	EPA Methods [3]	Standard Methods 15th Ed. [4]	ASTM Methods [5]	USGS Methods [6]	Other Approved Methods [7]
Chlorinated hydrocarbons						
1,2-dichlorobenzene	GC	601,602,612	--	--	--	--
	GC/MS	624,625, 1625	--	--	--	--
1,3-dichlorobenzene	GC	601,602,612	--	--	--	--
	GC/MS	624,625, 1625	--	--	--	--
1,4-dichlorobenzene	GC	601,602,612	--	--	--	--
	GC/MS	624,625, 1625	--	--	--	--
1,2,4-trichlorobenzene	GC	612	S102	--	--	b,130
	GC/MS	625,1625	--	--	--	--
Hexachlorobenzene	GC	612	--	--	--	f,10A-1
	GC/MS	625,1625	--	--	--	--
Hexachlorocyclopentadiene	GC	612[11],1624	S73	--	30	--
	GC/MS	625[11],1624	--	--	--	--
All others[9]	GC	612	--	--	--	--
	GC/MS	625,1625	--	--	--	--
Dioxin (TCDD)	GC/MS	613	--	--	--	--
Metals						
Antimony	0.45 µ filtration[14], followed by digestion[15], followed by AA[16] or ICP	204.1,204.2 (8)	S03A,304 (152,166)	D3697 (283)	--	d,5-34

(Continued)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class [1]	Method [2]	EPA Methods [3]	Standard Methods 15th Ed. [4]	ASTM Methods [5]	USGS Methods [6]	Other Approved Methods [7]
Metals (Cont.)						
Arsenic	0.45 μ filtration[14], followed by digestion, followed by silver diethyldithiocarbamate or AA[16,17] or ICP[18]	206.2,206.3 206.4,206.5	303E,307B (160,174)	D2972 (288)	47	a,564,387;c,3-110; d,5-34a,35;e,31,37
Beryllium	0.45 μ filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Aluminon) or ICP[18]	210.1,210.2	303C,309B (157,178)	D3645 (298)	33	d,5-37,38
Cadmium	0.45 μ filtration[15], followed by digestion[15], followed by AA[16] or colorimetric (Dithizone) or ICP[18]	213.1,213.2	303A,310B (152,180)	D3557 (313)	62	a,557;c,3-77;d,5-43
Chromium	0.45 μ filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Diphenylcarbazide) or ICP[18]	218.1,218.2 218.3,218.4	303A,312B (152,187)	D1687 (370)	78,77	a,557;c,3-77;d,5-56
Copper	0.45 μ filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Neocuproine) or ICP[18]	220.1,220.2	303A,313B (152,191)	D1688 (386)	83	a,557;c,3-77;d,5-58, 60
Lead	0.45 μ filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Dithizone) or ICP[18]	239.1,239.2	303A,316B (152,207)	D3559 (450)	105	a,557;c,3-77;d,5-72, 74

(Continued)

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Table 6 (Continued)

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Metals (Cont.)						
Mercury	0.45 u filtration[14], followed by flameless AA	245.1,245.2 245.5	303F (164)	D3223 (476)	-	a,559;c,3-118;d,5-81; e,31
Nickel	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Heptoxime) or ICP[18]	249.1,249.2	303A (152)	D1886 (488)	115	c,3-77;d,5-83
Selenium	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or ICP[18]	270.2,270.3	303E (160)	D3859 (542)	-	c,3-127;d,5-100
Silver	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Dithizone) or ICP[18]	272.1,272.2	303A,324B (152,227)	D3866 (556)	142	a,557;d,5-104
Thallium	0.45 u filtration[14], followed by digestion[15], followed by AA[16]	279.1,279.2	303A (152)	-	-	-
Zinc	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Dithizone) or ICP[18]	289.1,289.2	303A,324C (152,242)	D1691 (609)	159	a,557;c,3-77; d,5-116,117
Miscellaneous						
Total cyanides	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric	335.2,335.3	412H+(C;D) (317,319,320)	D2036 (701)	85	d,5-4;

(Continued)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class[1]	Method[2]	EPA Methods[3]	Standard Methods 15th Ed.[4]	ASTM Methods[5]	USGS Methods[6]	Other Approved Methods[7]
Miscellaneous (Cont.)						
Asbestos (fibrous)[11]	-	-	-	-	-	-
Other contaminants						
Metals						
Iron	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (Phenanthroline) or ICP[18]	236.1,236.2	303A,315B (152,201)	D1068 (438)	102	a,557;c,3-77; d,5-68,69,71
Manganese	0.45 u filtration[14], followed by digestion[15], followed by AA[16] or colorimetric (persulfate or periodate) or ICP[18]	243.1,243.2	303A+319B (152,214)	D858 (465)	111	a,557,564;c,3-77; d,5-79,80,81
Hydrogen ion (pH)	Electrometric measurement	150.1	423 (402)	D1293 (219)	129	a,547;c,3-48;d,5-91
Organophosphorous pesticides						
Diazinon	GC	-	551	-	24,30	b,25;c,3-319;d,5-133; f,10A-1

(Continued)

(Sheet 9 of 12)

Table 6 (Continued)

Chemical Contaminant or Contaminant Class [1]	Method [2]	EPA Methods [3]	Standard Methods 15th Ed. [4]	ASTM Methods [5]	USGS Methods [6]	Other Approved Methods [7]
Other contaminants (Cont.) **Organophosphorous pesticides (Cont.)**						
Guthion (azinphos methyl)	GC	-	S51	-	-	b,25;c,3-319;d,5-133; f,10A-1
Malathion	GC	-	509A[13],S51 (493)	-	24,30	b,25;c,3-319;d,5-133; f,10A-1
Parathion	GC	-	509A[13],S51 (493)	-	24,30	b,25;c,3-319;d,5-133; f,10A-1
Organochlorine pesticides						
Methoxychlor	GC	-	509A,S73 (493)	D3086 (765)	24,30	b,7;c,3-289;d,5-131; f,10A-1
Mirex	GC	-	509A (493)	D3086 (765)	-	b,7;c,3-289;d,5-131; f,10A-1
Chlorinated phenoxy acid herbicides						
2,4-D	GC	-	509B (503)	D3478 (738)	35	b,115;c,3-260;d,5-126;f,10A-1,10B-1
2,4,5-TP (Silvex)	GC	-	509B (503)	D3478 (738)	35	b,115;c,3-260;d,5-126;f,10A-1,10B-1
Kepone[11]	-	-	-	-	-	-

(Continued)

[1] Refer to Table 3 for a listing of the individual chemical contaminants associated with each of the contaminant classes shown in this table. Compounds listed under "Other Contaminants" in this table are those listed at the end of Table 2 (i.e., following zinc), which are not included in the 1980 EPA criteria (i.e., the List of 65) or in the expanded list of priority pollutants (Table 3).

[2] Symbols for analytical methods are as follows: GC - gas chromatography; GC/MS - gas chromatography/mass spectrometry; HPLC - high pressure liquid chromatography; AA - atomic absorption spectroscopy; and ICP - inductively coupled plasma optical emission spectroscopy.

Table 6 (Continued)

3   Numbers shown in this column refer to appropriate analytical methods approved by the EPA and published in US EPA (1979b), in the case of inorganic analyses, or in Longbottom and Lichtenberg (1982) and the Federal Register (1984), in the case of organic analyses.

4   Numbers shown in this column which are not preceded by an S refer to appropriate analytical methods contained in the 15th edition of Standard Methods (APHA 1981a). Shown in parentheses below the method number is the corresponding page number. Those numbers preceded by an S are page number references to methods contained in the Supplement to the 15th edition of Standard Methods (APHA 1981b). This Supplement lists those methods approved and cited by the EPA.

5   Numbers shown in this column refer to appropriate analytical methods contained in ASTM (1982). Associated page number references are shown below the method number in parentheses.

6   Numbers shown in this column refer to page numbers of appropriate USGS methods contained in Brown, Skougstad, and Fishman (1970), in the case of inorganic analyses, or in Goerlitz and Brown (1972), in the case of organic analyses.

7   Shown in this column are references to other approved and acceptable methods available for the indicated contaminants. Each reference is given as a source letter code and a page number, separated by a comma. Letter codes refer to the following sources: a - AOAC (1980); b - US EPA (1978); c - Plumb (1981); d - USGS (1977); e - Fishman and Brown (1976); f - US EPA (1980).

8   The purgeables listed in Table 3 were split into two groups to correspond with the EPA 600 Series Methods. Purgeable aromatics include benzene, chlorobenzene, toluene, and ethylbenzene. Purgeable halocarbons include all other contaminants listed in class I.A. purgeables in Table 3.

9   "All others" refers to all other compounds in this class in Table 3 which have been listed separately in this table; the methods shown apply to all compounds grouped in the "All Others" listing. If a common set of methods applies to all compounds in a class as listed in Table 3 (e.g., as in the case of phthalate esters), then the methods are listed by the class designation, and individual contaminants are not listed.

10 Method 624 may be employed to screen samples for the presence of acrolein and acrylonitrile. When they are known to be present, however, Method 603 is the preferred method for these two contaminants (Longbottom and Lichtenberg 1982).

11 Method 625 may be employed for benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodiphenylamine. When they are known to be present, however, Methods 605, 612, 607, and 607, respectively, are the preferred methods for these four contaminants (Longbottom and Lichtenberg 1982).

12 Several compounds included in the listings of priority pollutants in US EPA (1982) and in Mills et al. (1982) are not listed as being quantifiable by the EPA 600 Series Methods (Longbottom and Lichtenberg 1982) or by other methods manuals consulted in the preparation of this table. The EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, should be contacted for recommendations on appropriate analytical methods.

13 These pesticides may be determined by Method 509A of APHA (1981a) as indicated, under favorable circumstances. However, the identity of the pesticide in the sample must be confirmed by the analyst.

(Continued)

Table 6 (Concluded)

14 Dissolved metals are defined as those constituents which pass through a 0.45-um membrane filter. Samples for the determination of dissolved metals should thus be filtered prior to preservation and analysis. For the determination of total metals concentration, the sample is not filtered prior to preservation and analysis. Refer to Method 301A of APHA (1981a) or to Method 4.1.1 in the Metals Section of US EPA (1979b). Procedures for analyzing metals associated with the suspended fraction retained on the filter are also given in the referenced manuals.

15 Because vigorous digestion procedures may result in the loss of certain metals through precipitation, a less vigorous treatment is recommended, as given in Method 4.1.4 of the Metals Section in US EPA (1979b) (see also Method 301A of APHA (1981a) for comparable procedure). In those instances where a more vigorous digestion is required, the procedure given in Method 4.1.3 of the Metals Section of US EPA (1979b) should be followed (again consult Method 301A of APHA (1981a) for a comparable procedure).

16 Since the various furnace devices (flameless AA) are essentially atomic absorption methods, they are considered by the EPA to be approved test methods. Methods of standard addition are to be followed as noted in Method B.5 of the Metals Section of US EPA (1979b).

17 Refer to "Atomic Absorption Newsletter," Vol 13, No. 75 (1974). Available from Perkin Elmer Corporation, Main Avenue, Norwalk, CO 06852.

18 ICP methods are published by the EPA in the Federal Register (1984), Vol 49, pp 43431-43436.

Table 7

Characteristics of Select General Purpose

Data Base Management Systems*

System	Vendor	Computer Hardware for Which System Is Designed	Comments on System Characteristics
STORET	US EPA	IBM	System difficult to use for computer novice. Extensive water quality data base maintained. No quality assurance controls on stored data. Can access special purpose management systems (SAS).
WATSTORE	USGS	AMDAHL	Access restricted by USGS. Extensive water quality data base maintained. Data reliability enhanced by careful data verification procedures. System provides limited access to statistical and mathematical algorithms for data analysis but advanced graphics capabilities.
AURAS	CE-ORD	UNIVAC 1108 (via Computer Science Corp. INFONET system)	System provides ability to augment current CE water quality data bases. Provides limited statistical analysis and graphical and tabular data display routines.
SIR (Scientific Information Retrieval System)	SIR, Inc.	CDC 7600 (Boeing Computer Services Corp.)	An advanced data storage and retrieval system. No nationwide water quality data base maintained. System provides good analytical capabilities and access to several special purpose management systems (SPSS, BMDP).
UPGRADE	CEQ	Available on several commercially available computer networks	System provides access to an existing water quality data base. Contains an English language-prompting command structure; thus, easy to use by the computer novice. Can access special purpose management systems (SAS).
NAWDEX	USGS	Available on computer system at USGS National Center, Reston, VA	System easy to use with good prompts. Water quality data base maintained. USGS assists users in information retrieval.

* Summarized from information in EM 1110-2-1201.

Table 8

Characteristics of Select Special Purpose

Data Base Management Systems*

System	Vendor	Programing Allowed	Graphics Capabilities	Comments on System Characteristics
BMDP (Biomedical Statistical Package)	BMDP Statistical Software Los Angeles, CA	Limited	None	A reliable and comprehensive system with 22 years of operational history. Provides over 40 specific statistical analysis routines. Has limited data storage and retrieval capabilities. Thus, best used with a general purpose system.
SPSS (Statistical Package for the Social Sciences)	SPSS Inc. Chicago, IL	No	Limited	Provides a wide array of statistical routines. Especially good for multivariate statistics. Both batch (SPSS) and conversational (SCSS) versions available. Has limited data storage and retrieval capabilities. Thus, best used with a general purpose system.
IMSL (International Mathematical and Statistical Libraries)	IMSL Inc. Houston, TX	Limited	Limited	Contains the most complete set of mathematical and statistical routines available. Over 500 subroutines included. A FORTRAN-based system. Contains no data storage and retrieval capabilities. Use with a general purpose system mandatory.
MINITAB	Minitab Project, Pennsylvania State University	?	Limited	The most recent system to be marketed. A customized system which can be used on many different computer systems. Provides limited statistical routines. Inexpensive to use; has easy access commands. Has limited data storage and retrieval capabilities. Thus, best used with general purpose system.

(Continued)

* Summarized from information in EM 1110-2-1201.

Table 8 (Concluded)

System	Vendor	Programming Allowed	Graphics Capabilities	Comments on System Characteristics
SAS (Statistical Analysis System)	SAS Institute Raleigh, NC	Yes	Advanced color graphics	The most complete special purpose system marketed. Provides a wide array of statistical and mathematical routines for data analysis. Can be interfaced with other special purpose systems. Contains an easy-to-use language command set. Thus, minimal training required. Provides reliable data base management via interfacing with IBM's Information Management System.

Table 9

Hypothetical Data (units of micrograms per litre) on Concentrations of Some Contaminant in Random Water Samples from a Specific Reservoir*

Population 1

Sample concentrations: 48, 66, 31, 72, 104, 52, 60, 72, 0, 0, 0, 18, 0, 66, 47, 62, 4, 0, 40, 80, 71, 58, 38, 0, 0, 61

Summary statistics:

$n = 26$ $\bar{X} = 40$

$s^2 = 1001$ $s = 32$

$s_{\bar{X}} = 6$

Population 2

Sample concentrations: 135, 132, 62, 145, 169, 104, 120, 144, 0, 0, 0, 0, 37, 0, 131, 94, 125, 7, 0, 79, 161, 142, 117, 75, 0, 0

Summary statistics:

$n = 26$ $\bar{X} = 81$

$s^2 = 3792$ $s = 62$

$s_{\bar{X}} = 12$

* Data presented for two seperate sample populations in relation to a water quality standard of 100 µg/ℓ.

Table 10

Summary of Processes Regulating the Environmental Behavior of Contaminants Which are Considered in the EPA Screening Procedures*

Process Category	Individual Process	Level of Analysis at which Process Considered	Process Relevant to Toxic Metals?	Process Included in Reservoir Specific Methods?
Transport	Advection	First	Yes	Yes
	Precipitation-dissolution	Second	Yes	No
	Sedimentation	Second	Yes	Yes
	Solubility	Second	Yes	No
	Volatilization	Second	No	Yes
Speciation	Acid-base reactions	Second	Yes	No
	Sorption	Second	Yes	Yes
Transformation	Biodegradation	Third	No	Yes
	Hydrolysis	Third	Yes	Yes
	Oxidation-reduction	Third	Yes	No
	Photolysis	Third	No	Yes
Bioaccumulation	Bioconcentration	Fourth	Yes	Yes
	Biomagnification	--**	Yes	No

* Information summarized from Mills et al. (1982).
** Process not explicitly included in screening methods.